AMERICAN SCIENCE SERIES—ADVANCED COURSE

# INORGANIC CHEMISTRY

BY

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# PREFACE TO THE FIRST EDITION.

In the preparation of this book I have been much encouraged by the cordial reception which has been given my earlier text-books, both in this country and abroad. While those earlier works are intended to form a series of which the present volume is the most advanced member, it has little in common with the lower members except the general method of treatment. An occasional paragraph from the "Briefer Course" has been incorporated, but the two books are quite distinct.

In classifying the elements the periodic system has been adopted, and this has been pretty closely adhered to. In order to secure as logical treatment as possible it has been thought best not to give detailed descriptions of apparatus and specific directions for the preparation of substances, in the text proper. By avoiding these the attention can be better directed to the principles involved and a clearer conception of these principles will be formed, than when the attention is distracted by the reading of such details. On the other hand, full descriptions of apparatus and processes will be found in the Appendix ; and these, it is believed, will be of service to the teacher in the lecture-room, as well as to the student in the laboratory.

The feature of the book which perhaps most distinguishes it from others is the fulness with which general relations are discussed in it. Attention is constantly called to analogies between properties of substances and between chemical reactions, so that the thoughtful student will, it is hoped, be led to look upon the substances and the reactions not as independent of one another, but as related in many ways, and thus forming

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parts of a system. All thinking chemists have no doubt at times an indistinct vision of a perfect science of Chemistry yet to come, in which the relations of the parts will be clearly seen, and in which much that now appears of little or no importance will be recognized as significant. The subject cannot as yet, however, be treated as if that perfection had been reached. Much progress has been made of late years in the classification of the facts, and it is of prime importance to the student that general relations should be pointed out for him as clearly as possible.

Of course in the classification of facts the end is not reached. In every case of chemical action there are certain features which call for much deeper study than is usually given to them. For the most part chemists have been content to know what chemical changes take place when two or more substances are brought into action, and have paid much less attention to the accompanying phenomena; and yet it is evident that, in order to get a clear conception of the nature of the chemical act, it is necessary that we should learn all we possibly can in regard to that act. Of late years more and more attention has been given to the study of the phenomena accompanying chemical changes; and a clearer view has been gained regarding chemical action. A great field of study is thus opened, which bears to the science of Chemistry as a whole somewhat the same relation that Physiology bears to Biology, while the study of chemical substances and their changes as usually carried on is in the same way the counterpart of Morphology. Neither of the parts taken separately is Chemistry in the fullest sense. It will never be possible to study Chemistry without taking up and working with chemical substances; but as knowledge grows, more and more attention will surely be given to chemical action. In this book considerable space is devoted to the discussion of the results obtained in the latter kind of study. Some, no doubt, will hold that even more prominence should have been given to this side of the subject. Indeed I shall be glad if some of those who use the book become interested in the new problems,

and go further into their study. It has not, however, appeared to me advisable, considering the purposes for which this book has been written, to discuss them more fully.

The subject of the Constitution of Chemical Compounds receives a due share of attention. Constitutional formulas are not, however, used recklessly as though they were provided by nature ready-made; but the effort is made to keep clearly in mind the facts which they express so that they may be used intelligently. In this connection I may call special attention to the way in which the constitution of the so-called double salts of the halogens is treated. To those who have not carefully looked into the evidence, the formulas used will perhaps appear too speculative. I should be sorry to err in this direction. For some time past the view put forward has seemed to me to be justified, and I find that others whose judgment I respect have held the same view at least in regard to some of the compounds in question. As, generally speaking, these compounds are treated inadequately, and as they are commonly regarded as inexplicable, I propose soon to present, in the proper place, the evidence upon which my present view rests, when it will, I think, be found that the evidence is fully as strong as that upon which our views concerning the constitution of most compounds are founded.

IRA REMSEN.

BALTIMORE, *March*, 1889.

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## PREFACE TO SECOND EDITION.

THE call for a new edition of this book has given me an opportunity to make some desirable changes, and to correct those errors to which my attention has been directed by others or which I have myself discovered. The revision is based upon the labors of a very consid-

erable number of readers who have given me the benefit of their criticisms, and I take this opportunity to express my sincere thanks to all those who have aided me. Should any one using the new edition discover errors in it, I shall be thankful to be informed of the fact. It seems fair to say that I have heard only words of commendation in regard to the general plan and spirit of the book.

<div align="right">IRA REMSEN.</div>

BALTIMORE, *December 6*, 1889.

## PREFACE TO FIFTH EDITION.

DURING the eight years that have passed since the second edition of this book was published a number of minor corrections have been made in it from time to time. It has now, however, been subjected to a thorough revision, and it is hoped that this new edition will be found to contain everything that can fairly be looked for in a book of its size. A new Appendix has been added containing much information concerning the properties of a large number of compounds which are necessarily treated briefly or not at all in the text.

It may not be inappropriate to mention the fact that the book has been well received not only in this country, but in England and in Germany, a German translation having appeared shortly after the publication of the first American edition.

<div align="right">IRA REMSEN.</div>

BALTIMORE, *February* 21, 1898.

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# A TEXT-BOOK OF

# INORGANIC CHEMISTRY.

## CHAPTER I.

CHEMICAL AND PHYSICAL CHANGE—EARLIEST CHEMI-
CAL KNOWLEDGE—LAW OF THE INDESTRUCTIBILITY
OF MATTER—LAW OF DEFINITE PROPORTIONS—LAW
OF MULTIPLE PROPORTIONS—THE ELEMENTS.

**Matter and Energy.**—The sensible universe is made up
of matter and energy. It is difficult to give satisfactory
definitions of either of these terms, but, in a general way,
it may be said that matter is anything which occupies
space, and energy is that which causes change in matter.
It requires but little observation to show that there are
many kinds of matter, and apparently many kinds of
energy. As examples of the different kinds of matter we
have the many varieties of rocks and earth, as granite,
limestone, quartz, clay, sand, etc.; the plants and their
fruits; the substances which enter into the composition
of animals; and innumerable manufactured products.
As examples of the different forms of energy, we have
heat, light, motion, etc. Under the influence of the forms
of energy the forms of matter are constantly undergoing
change. Everywhere these changes are taking place.
Changes in position and in temperature appeal most
directly to our senses, and are most easily studied. But
there are many other kinds of change which are of the
highest importance. Thus there are electrical changes,
manifestations of which we see in thunder-storms; there
are magnetic changes which may be studied to some ex-
tent by means of the magnetic needle; and there are,
further, what are called chemical changes which affect
the composition of substances.

**Chemical Change.**—For the purpose of study it is convenient to distinguish between two classes of changes in matter, the difference between which can best be made clear by means of examples. Consider the changes included under the head of fire. We see substances destroyed by fire, as we say. They disappear as far as we can determine by ordinary observation. When iron is exposed to the air a serious change takes place. It becomes covered with a reddish-brown substance which we call rust. If the piece of iron is comparatively thin, and it be allowed to lie in the air long enough, it is completely changed to the reddish-brown substance, and no iron as such is left. If the juices from fruits, as from apples, be allowed to stand in the air, they undergo change, becoming sour, and a somewhat similar change takes place in milk. If a spark be brought in contact with gunpowder there is a flash and the powder disappears, a dense cloud appearing in its place.

In the changes referred to the substances changed disappear as such. After the fire, the wood or the coal, or whatever may be burned, is no longer to be found. The rusted iron is no longer iron. The gunpowder after the flash is no longer gunpowder. Changes of this kind in which the substances disappear and something else is formed in their place are known as *chemical changes.*

**Physical Change.**—There are many changes taking place which do not affect the composition of substances. Iron, for example, may be changed in many ways and still remain iron. It may become hotter or colder. Its position may be changed, or, as we say, it may be moved. The iron may be struck in such a way as to give forth sound. It may be made so hot that it gives light. When, for example, it becomes red-hot, it can be seen in a dark room. A piece of iron may be changed further by connecting it with what is known as a galvanic battery. A current of electricity then passes through it, and we can easily recognize the difference between a piece of iron through which a current of electricity is passing and one through which no current is passing. The former when brought into certain liquids will at once change

their composition, while the latter will not cause such change. Finally, when a piece of iron is brought in contact with loadstone, it acquires new properties. It now has the power to attract and hold to itself other pieces of iron. In all these cases, the iron is changed, but it remains iron. After the moving iron comes to rest, it is exactly the same thing that it was before it was moved. After the iron which is giving forth sound has ceased to give forth sound, it returns to its original condition. Let the heated iron alone, and it cools down, ceasing soon to give light, and presenting no evidence of being warm. Remove the iron from contact with the galvanic battery, and it loses those properties which are due to the current of electricity. In time, the iron which is magnetized by contact with the loadstone loses its magnetic properties. It then no longer has the power to attract other pieces of iron; and does not differ from ordinary iron.

While iron has been taken as an example, other substances undergo similar changes. These changes which do not affect the composition of the substances are called *physical changes.*

**Physics and Chemistry.**—According to what has been said, we have two classes of changes presented to us for study:

(1) Those which do not affect the composition of substances, or physical changes.

(2) Those which do affect the composition of substances, or chemical changes.

That branch of science which has to deal with physical changes is known as Physics. And that which has to deal with chemical changes is known as Chemistry.

Everything that has to do with motion, heat, light, sound, electricity, and magnetism, is studied under the head of Physics. Everything that has to do with the composition of substances is studied under the head of Chemistry. It is, however, impossible to study these two subjects entirely independently of each other. Whenever a chemical change takes place, it is accompanied by physical changes; and in order that the former may be clearly understood, a study of the latter is necessary.

**Earliest Chemical Knowledge.**—Those substances which are most abundant and most widely distributed in nature were, of course, the first known and studied; and the same is true of those chemical changes which occur most commonly and produce the most striking effects. Simply by observing those things which surround us and those changes in composition which take place naturally, a considerable amount of chemical knowledge might be gained, and indeed the earliest knowledge of chemistry was acquired in this way. It was not, however, until men came to experiment upon the substances which they found in nature, that knowledge of chemical changes made rapid progress. Since then an enormous amount of knowledge has been gained, and every year the stock is increased by new discoveries, until the field appears almost boundless.

**Alchemy.**—One of the first and one of the most powerful incentives to experiment upon chemical substances was the desire to transform ordinary metals like lead into gold. As will be seen farther on, there was no good reason to suppose that transformations of this kind could not be effected, indeed there were good reasons for supposing them possible. For many hundred years men worked with this object in view, and, though they did not succeed in accomplishing that which they undertook, they did add greatly to our knowledge of the action of chemical substances upon one another, and they laid the foundation of what has since become the great science of chemistry. The work done by the alchemists was necessary to prove that the transformations of matter which they tried to effect cannot be effected. The problem which they tried to solve was strictly a chemical problem, and the work they did was chemical work.

**Chemistry as a Science.**—While the alchemists accumulated a vast amount of knowledge of chemical facts, they did not, strictly speaking, build up the science of chemistry. It was only when chemists came to study the facts in their relations to one another, and when they were enabled to trace connections between them; when they succeeded in discovering that certain general truths hold

good for all cases of chemical action; when, in short, the fundamental laws of chemical action were discovered —it was then that knowledge became science. It is impossible to say definitely when chemistry became a science. From the unorganized state to the organized there was a gradual transition. But it is certain that the labors of the French chemist Lavoisier contributed largely to making chemistry what it is to-day, and it is common to refer to his work as the beginning of the science.

**Lavoisier's Work.**—What distinguished Lavoisier's work most markedly from that of his predecessors was the way in which he used the balance for the purpose of studying chemical changes. The balance had been used to a considerable extent by earlier workers and results of value had been reached by them, but Lavoisier succeeded by means of it in explaining some important chemical phenomena which had long been the subject of study. His first investigation, the results of which were published in 1770, was on the transformation of water into earth. It was generally believed that water is transformed into earth by boiling, because it was a matter of common observation that, whenever water is boiled for a time in a glass vessel, a deposit of earthy matter is formed. In order to decide whether such transformation takes place or not, Lavoisier boiled some water in a closed vessel which he weighed before and after the boiling; and he found that the vessel decreased in weight by a certain amount. He also determined the weight of the deposit formed in the vessel and found that this was exactly equal to the loss in weight of the vessel. He also showed that there was just as much water after the experiment as before. He therefore concluded that what his predecessors had held to be a transformation of water into earth was nothing but a partial disintegration of the glass vessel caused by the action of the boiling water. What had appeared mysterious became clear and simple. Having succeeded so well in this experiment, Lavoisier proceeded to study other chemical changes in the same way, and soon he was able to give a perfectly satis-

factory explanation of the process of combustion which for a long time had been a subject of study. The explanation and the experiments which led to it will be taken up later. Suffice it to say here that the essential feature of the work consisted in the fact that the substances which entered into action and those formed during the action were all carefully weighed, and it was found, in every case, that the weight of the substances formed was exactly equal to the weight of the substances which acted upon one another.

**Law of the Indestructibility of Matter.**—While, as has been stated, chemists before Lavoisier had used the balance, they do not appear to have been very strongly impressed by the importance of the weight of substances. They seem tacitly to have held that matter can be destroyed. Lavoisier's work, however, showed that whenever matter apparently disappears, it continues to exist in some other form. If it were possible to annihilate matter or to call it into being, it would be of little or no value to weigh things. Innumerable experiments which have been performed since Lavoisier's time have confirmed the view that matter is indestructible. The first fundamental law bearing upon the changes in composition which the different forms of matter undergo is the *law of the indestructibility of matter.* While, if we think of it, we can scarcely conceive that this great law should not be true, we must not forget that the only way in which its truth could be established was by experiment. The law may be stated thus:

*Whenever a change in the composition of substances takes place the amount of matter after the change is the same as before the change.*

According to this, and assuming that the law has always held good, it follows that the amount of matter in the universe is the same to-day as it has been from the beginning. Transformations are constantly taking place, but these involve no increase nor decrease in the total amount of matter.

**Conservation of Energy.**—Just as matter is neither created nor destroyed, so it has been made probable that

the total amount of energy is unchangeable. One of the greatest discoveries in science was the recognition of the fact that one form of energy can be transformed into others, and that in these transformations nothing is lost. We now know that for a certain amount of heat we can get a certain amount of motion, and that for a certain amount of motion we can get a certain amount of heat. We know that a similar definite relation exists between heat and electrical energy, and between these and chemical energy. We know, for example, that a definite amount of heat can be obtained by burning a definite amount of a given substance, and we know also that with a definite amount of heat we can produce a definite amount of chemical change. Modern investigation has shown that all the different forms of energy are convertible one into the other without loss. This great fact is generally spoken of as the *law of the conservation of energy.* Transformations of energy are taking place constantly, as transformations of matter are, but the total amount in each case remains the same.

**Early Views regarding the Composition of Matter.**— The fact that first impresses one in studying the various forms of matter found in the earth is their great variety. We find an almost infinite number of kinds of matter, and the question at once suggests itself, of what are these things composed? This question has long been asked, and it will be long before an entirely satisfactory answer is reached. Still, much more is now known in regard to the subject than was known in past ages, and some progress is constantly being made towards a solution of the problem. At first, men attempted to answer the question, as they attempted to answer all important questions, by what is known as the speculative method; that is to say, they took the facts, as far as they knew them, into consideration, and they endeavored by purely mental processes to furnish an explanation. They were on the whole much bolder in the use of the imagination than the scientific men of the present are, or rather they do not appear to have had as great respect for facts as men now have, and, as a consequence, we find that some

extremely curious speculations were indulged in. One
of the most prominent views in regard to the composi-
tion of matter was that put forward by Aristotle. Ac-
cording to this view, all forms of matter are made up of
four elements, earth, air, fire, and water; and the vari-
ous forms differ from one another in the proportions of
these elements contained in them. Aristotle evidently
had in mind the fundamental properties of the four ele-
ments, rather than the elements themselves, and his idea
was that these fundamental properties are found in dif-
ferent proportions. Instead of meaning that water as
such was contained in substances, he meant that the
properties of cold and moisture were met with in sub-
stances, and so on for the other elements; fire repre-
senting heat and dryness; earth, cold and dryness; and
air, heat and moisture. Afterwards it was pointed out
that besides the four fundamental properties represented
by the four elements, each substance has a special prop-
erty of its own which distinguishes it from all others.
This was called the *quinta essentia*, or fifth essence, from
which our modern word quintessence is derived. The
four or five elements of the older philosophers were, as
will be seen, imaginary things. They represented ideas
rather than tangible substances.

**Elements.**—As experimenting upon chemical substances
advanced further and further, the fact impressed itself
more and more strongly upon investigators, that, of the
large number of substances known, some can be con-
verted into simpler ones by chemical action and some
cannot. In other words, some substances like water
can be broken down by various methods into two or
more others of different properties, and these when
brought together again under proper conditions form
the original substance. In the case of water, the action
of an electric current breaks it down or decomposes it,
and two gases, hydrogen and oxygen, are formed from it.
Elaborate experiments have shown that the weight of
water decomposed is exactly equal to the weight of the
hydrogen plus that of the oxygen obtained, and that
when the hydrogen and oxygen are brought together

again under proper conditions exactly as much water is formed as was originally decomposed. It appears, therefore, that water consists of at least two simpler substances. A similar conclusion is reached by a study of by far the largest number of the substances with which we have to deal. On the other hand, no treatment to which hydrogen and oxygen have been subjected has, as yet, effected their decomposition. They can be made to combine with other substances, as, for example, with each other, and thus form more complex substances, but nothing simpler than hydrogen has ever been obtained from hydrogen, and nothing simpler than oxygen has ever been obtained from oxygen. Whether the decomposition of these substances will ever be effected is a question which cannot be answered. All that we know is that at present they cannot be decomposed. We therefore speak of them as elements, meaning by the term, that, with the means now at the disposal of chemists, it is impossible to get simpler substances from them. There are at present about seventy substances known which are called elements for the same reasons that hydrogen and oxygen are called elements. It is quite possible that the number may be increased in the future, and it is also quite possible that the number may be decreased. New elements will in all probability be discovered, and probably some of the substances now included in the list of elements may eventually be shown to be capable of decomposition.

The view at present held in regard to the forms of matter which go to make up that part of the universe which comes under our observation is that they are all composed of the seventy elementary substances. Many of them, like water, are composed of only two elements; others of three; and still others of four, five, six, and more; but most of them are comparatively simple, and rarely does any one contain more than four or five elements. Of the seventy elements known, only about twelve enter into the composition of most things with which we commonly have to deal. The others occur in relatively small quantity.

**Chemical Action.**—In the last paragraph it was stated that most substances can be decomposed, and that under proper conditions the elements combine. We must now inquire more carefully into the meaning of these expressions. Among the elements are the well-known substances lead, iron, and sulphur. If some finely divided iron is brought in contact with sulphur, apparently no action takes place. If the two are put in a mortar and mixed no matter how thoroughly, there is no evidence of action. The mixture has, to be sure, a different appearance from that of either constituent, but still both substances are present, and can be recognized by various methods. If, for example, a little of the mixture is examined with the aid of the microscope, particles of iron and of sulphur will be recognized lying side by side. If, further, the mixture is treated with the liquid, carbon disulphide, which has the power to dissolve the sulphur but not the iron, the sulphur will be dissolved while the iron will be left unchanged. Finally, if a dry magnet is introduced into the mixture, the iron will adhere to it, and by careful manipulation the two constituents can be separated. These facts furnish evidence that both iron and sulphur are present in the mixture in unchanged condition, just as sugar and sand are present in a mixture of these two substances. If now the mixture of sulphur and iron is heated in a dry test-tube, marked changes will take place, and there will be formed a black substance entirely different from either of the elements employed in the experiment. Carbon disulphide can no longer extract sulphur from it. The magnet can no longer pick out the iron, and under the microscope one homogeneous substance is seen instead of the two elementary substances. If the experiment is performed with proper precautions, the amount of matter after the action will be found to be exactly the same as before the action. A serious change has taken place, but no change in the amount of matter. The act is one of chemical combination, and the substance formed is called a *chemical compound*. A few other examples will aid in making the conception of chemical combination clear. When a bit

of phosphorus is brought in contact with a little iodine action takes place at once; the two elements combine, losing their own characteristic properties and forming a compound with properties quite different from those of the constituents. When the gases hydrogen and oxygen are brought together and a spark is passed through the mixture an explosion occurs, and, in place of the gases, the liquid, water, is formed. When sulphur burns in the air the product formed is a pungent gas. It has been shown that the act consists in the combination of the sulphur with the gas, oxygen, which is contained in the air. All these cases are examples of chemical combination. But chemical action may be of the opposite kind, that is to say, instead of being *combination*, it may be *decomposition*. Thus, water which is formed by the chemical combination of hydrogen and oxygen may, by proper methods, be decomposed into the same elements. We may conveniently think of that which causes elements to combine as an attractive force exerted between the elements. Now, when some power which can overcome this attraction is brought to bear upon a compound, decomposition takes place, and the elements are, as we say, set free. When, for example, an electric current is passed through water, the power which holds together the hydrogen and oxygen is overcome and bubbles of the one gas rise from one pole of the battery and bubbles of the other gas rise from the other pole. This is a simple example of chemical decomposition. Again, when the substance known as red oxide of mercury or mercuric oxide is heated to a sufficiently high temperature a colorless gas is given off from it, and globules of mercury are formed at the same time. The gas, as will be shown later, is oxygen, so that from the red oxide of mercury, which is a chemical compound of mercury and oxygen, we get, by heating, the two elements in the free state. In this case, heat overcomes the chemical attraction which, in the compound, holds the elements together.

**Chemical Affinity.**—It is evident from what has already been said that there is some power which can hold substances together in a very intimate way, so intimate that

we cannot recognize them by ordinary means. We do not know what causes the sulphur and iron to combine, but we do know that they combine. Similarly, we do not know what causes a stone thrown in the air to fall back again, but we know that it falls back. It is true we may say that the cause of the falling of the stone is the *attraction of gravitation,* but this does not give us any real information, for, if we ask what the attraction of gravitation is, we can only answer that it is that which causes all bodies to attract one another. We may also say, and do say, that the cause of chemical combination is *chemical affinity*. But in so doing we only give a name to something about which we know nothing except the effects it produces. All the chemical changes which are taking place around us may, then, be referred to the operation of chemical affinity. If this power should cease to operate, what would be the result? Nature would be infinitely less complex than it now is. All complex substances would be resolved into the elements of which they are composed, and, as far as we know, there would be only about seventy different kinds of substances. All living things would cease to exist, and in their place there would be three invisible gases, and something very much like charcoal. Mountains would crumble to pieces, and all water would disappear giving two invisible gases. The processes of life in its many forms would be impossible, as, however subtle that which we call life may be, we cannot imagine it to exist without the existence of certain complex forms of matter; and, as regards the life process of animals and plants, most complex chemical changes are constantly taking place within them, and these changes are essential to the continuance of life.

**Chemical Compounds and Mechanical Mixtures.**—The substances formed by chemical combination of the elements are called chemical compounds. Most substances found in nature are made up of several others. Wood, for example, is very complex, containing a large number of distinct chemical compounds intimately mixed together. Some of these can be isolated, but it is impossible to isolate them all with the means at present at our com-

mand. Most of the rocks met with are also quite complex, and it is difficult to isolate the constituents. If we look at a piece of coarse-grained granite, we see plainly enough that it contains different things mixed together, and if it be broken up we can pick out pieces of different substances from the mass. If we now examine a piece of each of the different substances thus picked out of the granite, it appears to be homogeneous, i.e. we cannot recognize the presence of more than one kind of thing in any one piece. If the piece is carefully selected it may be powdered finely in an agate mortar, and some of the powder examined with a microscope without the presence of more than one substance being recognized. We are able to isolate three substances from granite by simply breaking it up and picking out the pieces of different kinds. We might therefore conclude that granite consists of three substances. This is true, but it is not the whole truth. For it is possible by proper means to get simpler substances from each of the three already separated. This is, however, a much more difficult process than the separation first accomplished. To effect the separation of each of the three constituents of granite into its elements requires more powerful means. Substances must be brought in contact with them which act upon them, changing their composition, i.e. act chemically upon them, and high heat must be used to aid the action. By skilful work it is, however, possible to separate the three components of granite into their elements.

From the above it is evident that substances may be united in different ways. They may be so united that it is a simple thing to separate them by mechanical processes. Or they may be so united that it is impossible to separate them by mechanical processes. By a mechanical process is meant any process which does not involve the use of heat, electricity, or chemical change. Thus, the mechanical process made use of in the case of granite consisted in picking out the pieces. The separation of the particles of different sizes by means of a sieve is a mechanical process. The separation of two liquids which do not mix with each other is a mechanical process. Complex sub-

stances which may be separated into their components by purely mechanical processes are called mechanical mixtures. Thus granite is a mechanical mixture of three chemical compounds. Similarly, most natural substances are more or less complex mixtures of chemical compounds, or, much more rarely, of elements. Air, for example, is a mechanical mixture consisting mainly of the two elements nitrogen and oxygen. It is not always an easy matter to distinguish between mechanical mixtures and chemical compounds, as there are mixtures which it is extremely difficult to subdivide into their components, and there are, on the other hand, chemical compounds which are extremely unstable. Generally, however, the difference is recognized without serious difficulty.

**Qualitative and Quantitative Study of Chemical Changes.** —In general there are two ways in which chemical changes may be studied. Substances may be brought together under a variety of conditions and, if action takes place, the properties of the product or products may then be studied and compared with those of the substances brought together. In the early periods of the history of chemistry the study was almost wholly of this kind. This is called *qualitative study*. But we may go farther than this, and take into consideration the weights or masses of the substances we are dealing with. We should then be studying the changes *quantitatively*. We have already seen that by means of the quantitative method Lavoisier placed the law of the indestructibility of matter upon a firm basis, and that he also succeeded by the use of this method in explaining a number of important chemical changes, particularly combustion. By further use of this method other laws of the highest importance to the science of chemistry were soon brought to light.

**Law of Definite Proportions.**—The fact that sulphur and iron combine chemically when a mixture of the two is heated has been referred to. The question whether they combine in all proportions is one which can be answered only by a quantitative study of the process. If the process were to be studied for the first time the method of procedure would be this: We should mix the elements

in different proportions and, after the action, we should determine whether any of either of the elements is left in the uncombined state ; and, further, by decomposing the product, we should determine whether it always contains the elements in the same proportions. The problem, in this case, is by no means a simple one, but it has been repeatedly worked over with the greatest possible care, and, as the result of the work, the conclusion is justified that the product always contains the elements in exactly the same proportions. Similar work has been done for most other chemical compounds known, and the general conclusion known as the *law of definite proportions* has been drawn. This law may be stated thus :

*A chemical compound always contains the same constituents in the same proportion by weight.*

The truth of this general statement or law has not always been acknowledged by chemists. At the beginning of this century a celebrated discussion on the subject took place between Proust and Berthollet. The discussion led to a great deal of careful work which tended to confirm the law, and since that time it has not been seriously doubted. About twenty years ago a Belgian chemist, Stas, by a long series of probably the most painstaking and accurate chemical experiments ever performed, showed that in the compounds which he worked with there was no variation in composition that could be detected by the most refined methods of chemistry. In the present state of our knowledge it appears that the law of definite proportions is a law in the strictest sense.

**Law of Multiple Proportions.**—It does not require a very extended study of chemical phenomena to show that from the same elements it is possible in many cases to get more than one product. Thus iron and sulphur form three distinct compounds with each other. Tin combines with oxygen in two proportions. The elements potassium, chlorine, and oxygen combine in four different ways, forming four distinct products. Nitrogen and oxygen form five products. In the early part of this century the English chemist Dalton by a study of cases like those mentioned was led to the discovery of another great law of

chemistry known as the *law of multiple proportions.* Many substances had been analyzed before his time, and the percentages of the constituents determined with a fair degree of accuracy. He examined, first, two gases, both of which consist of carbon and hydrogen. He determined the percentages of the constituents, and found them to be as follows :

Olefiant gas, 85.7 per cent. carbon and 14.3 per cent. hydrogen.

Marsh gas, 75.0 per cent. carbon and 25.0 per cent. hydrogen.

On comparing these numbers, he found that the ratio of carbon to hydrogen in olefiant gas is as 6 to 1 ; whereas in marsh gas it is as 3 to 1 or 6 to 2. The mass of hydrogen, combined with a given mass of carbon, is exactly twice as great in the one case as in the other.

There are, further, two compounds of carbon and oxygen, and in analyzing these the following figures were obtained :

Carbon monoxide, 42.86 per cent. carbon and 57.14 per cent. oxygen.

Carbon dioxide, 27.27 per cent. carbon and 72.73 per cent. oxygen.

But 42.86 : 57.14 :: 6 : 8 and 27.27 : 72.73 :: 6 : 16.

The mass of oxygen combined with a given mass of carbon in carbon dioxide is exactly twice as great as the mass of oxygen combined with the same mass of carbon in carbon monoxide. These facts and other similar ones led to the discovery of the law of multiple proportions, which may be stated thus:

*If two elements A and B form several compounds with each other, and we consider any fixed mass of A, then the different masses of B which combine with the fixed mass of A bear a simple ratio to one another.*

By way of further illustration we may take the three compounds which iron forms with sulphur. In one of these, approximately 7 parts of iron are in combination with 4 parts of sulphur ; in a second, 7 parts of iron are in combination with 6 parts of sulphur ; and in the third, 7 of iron are in combination with 8 of sulphur. The figures

4, 6, and 8 bear a simple ratio to one another which is 2 : 3 : 4. The five compounds of nitrogen and oxygen contain 7 parts of nitrogen combined with 8, 16, 24, 32, and 40 parts of oxygen respectively. The figures representing the parts by weight of oxygen combined with 7 parts by weight of nitrogen are in the ratio 1 : 2 : 3 : 4 : 5. In the compounds formed by the elements chlorine, potassium, and oxygen the proportions by weight are represented in the following table:

| Chlorine. | Potassium. | Oxygen. |
|---|---|---|
| 35.18 | 38.82 | 15.88 |
| 35.18 | 38.82 | 31.76 |
| 35.18 | 38.82 | 47.64 |
| 35.18 | 38.82 | 63.52 |

It will be observed that the ratio between the chlorine and potassium remains constant, but that the mass of oxygen varies regularly from 15.88 to 63.52; the masses bearing to one another the simple ratio 1 : 2 : 3 : 4.

The law of multiple proportions like the law of definite proportions is simply a statement in accordance with what has been found true by experiment. Although discovered by Dalton at the beginning of this century and put forward upon what appears now to be only a slight basis of facts, all work since that time has confirmed it, and it forms to-day one of the corner-stones of the science of chemistry.

**Combining Weights of the Elements.**—A careful study of the figures representing the composition of chemical compounds reveals a remarkable fact regarding the relative quantities of one and the same element which enter into combination with different elements. The proportions by weight in which some of the elements combine chemically with one another are stated in the following table:

| | | | | | |
|---|---|---|---|---|---|
| 1 part Hydrogen combines with 35.18 parts Chlorine. | | | | | |
| 1 " | " | " | " | 79.34 " | Bromine. |
| 1 " | " | " | " | 125.89 " | Iodine. |
| 35.18 parts Chlorine combine " | | 38.82 " | Potassium. | | |
| 79.34 " | Bromine | " | " | 38.82 " | " |
| 125.89 " | Iodine | " | " | 38.82 " | " |

| 15.88 parts Oxygen | | combine | with | 64.91 | parts | Zinc. |
|---|---|---|---|---|---|---|
| 15.88 " | " | " | " | 24.10 | " | Magnesium. |
| 15.88 " | " | " | " | 39.76 | " | Calcium. |
| 15.88 " | " | " | " | 136.39 | " | Barium. |
| 64.91 " | Zinc | " | " | 31.83 | " | Sulphur. |
| 24.10 " | Magnesium | " | " | 31.83 | " | " |
| 39.76 " | Calcium | " | " | 31.83 | " | " |
| 136.39 " | Barium | " | " | 31.83 | " | " |

It will be seen that the figures which express the relative quantities of chlorine, bromine, and iodine that combine with 1 part of hydrogen also express the relative quantities of these elements that combine with 38.82 parts of potassium. So also the figures which express the relative quantities of zinc, magnesium, calcium, and barium that combine with 15.88 parts of oxygen also express the relative quantities of these elements that combine with 31.83 parts of sulphur. Now, an examination of all compounds known has shown that hydrogen enters into combination with the other elements in the smallest proportions ; it is therefore taken as unity in stating the relative quantities of the other elements which enter into combination. The weight of another element that combines with 1 part by weight of hydrogen may be called its *combining weight*. Thus, according to the above, the combining weights of chlorine, bromine, and iodine are respectively 35.18, 79.34, and 125.89. Similarly 38.82 is the combining weight of potassium, as it expresses the weight of potassium that combines with the above quantities of chlorine, bromine, and iodine. Thus for every element a number can be selected, such that the proportions by weight in which the element enters into combination with others can be conveniently expressed by the number or by a simple multiple of it. These numbers are the combining weights.

It is not by any means an easy matter to determine which numbers are most convenient for all circumstances ; and if the selection is to be determined solely by convenience, there may be differences of opinion as to what is most convenient. We shall see a little later that, while the numbers primarily express the combining

weights and nothing else, and are based solely upon a study of the composition of chemical compounds, they have come to have a deeper significance which will be explained in due time. They are now called *atomic weights* because for strong reasons they are believed to express the relative weights or masses of the minute indivisible particles or atoms of which the various kinds of matter are assumed to be made up. The atomic theory, as it is called, will be treated of farther on, and the relation which exists between the theory and the figures called the atomic weights will be discussed at some length. For the present it will be best to use the figures as expressing the combining weights, and as being entirely independent of any speculations regarding the constitution of matter and the existence of atoms.

**The Elements, their Symbols and Atomic Weights.**—It has already been stated that there are about seventy elementary substances known, but that of these only a small number enter into the composition of common things to any great extent. It has been calculated that the solid crust of the earth is made up approximately as represented in the subjoined table :

| | | | |
|---|---|---|---|
| Oxygen | 47.13% | Calcium | 3.53% |
| Silicon | 27.89% | Magnesium | 2.64% |
| Aluminium | 8.13% | Sodium | 2.68% |
| Iron | 4.71% | Potassium | 2.35% |

While oxygen forms a large proportion of the solid crust of the earth, it forms a still larger proportion (eight-ninths) of water, and about one-fifth of the air. Carbon is the principal element which enters into the structure of living things, while hydrogen, oxygen, and nitrogen also are essential constituents of animals and plants. Nitrogen forms about four-fifths of the air.

In representing the results of chemical action, it is convenient to use abbreviations for the names of the elements and compounds. Thus, instead of oxygen we may write simply O ; for hydrogen, H ; for nitrogen, N ; etc. These symbols are used in expressing what takes place when sub-

stances act upon one another. Very frequently the first letter of the name is used as the symbol. If the names of two or more elements begin with the same letter, this letter is used, and some other letter of the name is added. Thus, B is the symbol of boron, Ba of barium, Bi of bismuth; C is the symbol of carbon, Ca of calcium, Cd of cadmium, Ce of cerium, Cl of chlorine, Cr of chromium, Cs of cæsium, Cu of copper. In some cases the symbol is derived from the Latin name of the element. Thus, the symbol of iron is Fe, from the Latin *ferrum;* for copper Cu, from *cuprum;* for mercury Hg, from *hydrargyrum;* etc.

The names themselves are formed in a variety of ways. Chlorine is derived from the Greek χλωρός, which means yellowish-green, as this is the color of chlorine. Bromine comes from βρῶμος, a stench, a prominent characteristic of bromine being its bad odor. Hydrogen comes from ὕδωρ, water, and γένειν, to produce, signifying that it is a constituent of water. Similarly nitrogen comes from νίτρον, niter, and γένειν, to produce, nitrogen being one of the constituents of niter. Potassium is an element found in potash, and sodium is found in soda. Some elements have been named after the country in which they were first discovered. Thus we have gallium, discovered in France; scandium, discovered in Sweden; germanium, discovered in Germany. Tantalum was so called on account of the long-continued difficulties experienced in isolating it when it was discovered. Columbium received its name from the fact that it occurs in the mineral columbite, and this owes its name to the fact that it was first found in the United States of America.

Below is given a table containing the names of all the elementary substances now known, together with their symbols and atomic weights. The names of those which are most widely distributed, and form by far the largest part of the earth, are printed in SMALL CAPITALS. The names of those which are rare are printed in *italics*.

| Element. | Symbol. | Atomic Weight. | Element. | Symbol. | Atomic Weight. |
|---|---|---|---|---|---|
| ALUMINIUM | Al | 26.91 | Molybdenum | Mo | 95.26 |
| Antimony | Sb | 119.52 | *Neodymium* | Nd | 139.70 |
| *Argon* | A | (?) | Nickel | Ni | 58.24 |
| Arsenic | As | 74.44 | NITROGEN | N | 13.93 |
| Barium | Ba | 136.39 | *Osmium* | Os | 189.55 |
| Bismuth | Bi | 206.54 | OXYGEN | O | 15.88 |
| Boron | B | 10.86 | Palladium | Pd | 105.56 |
| Bromine | Br | 79.34 | Phosphorus | P | 30.79 |
| Cadmium | Cd | 111.10 | Platinum | Pt | 193.41 |
| *Cæsium* | Cs | 131.89 | POTASSIUM | K | 38.82 |
| CALCIUM | Ca | 39.76 | *Praseodymium* | Pr | 142.50 |
| CARBON | C | 11.92 | *Rhodium* | Rh | 102.23 |
| *Cerium* | Ce | 139.10 | *Rubidium* | Rb | 84.78 |
| CHLORINE | Cl | 35.18 | *Ruthenium* | Ru | 100.91 |
| Chromium | Cr | 51.74 | *Samarium* | Sm | 149.13 |
| Cobalt | Co | 58.49 | *Scandium* | Sc | 43.78 |
| *Columbium* | Cb | 93.02 | *Selenium* | Se | 78.42 |
| Copper | Cu | 63.12 | SILICON | Si | 28.18 |
| *Erbium* | E | 165.06 | Silver | Ag | 107.11 |
| Fluorine | F | 18.91 | SODIUM | Na | 22.88 |
| *Gadolinium* | Gd | 155.57 | Strontium | Sr | 86.95 |
| *Gallium* | Ga | 69.38 | Sulphur | S | 31.83 |
| *Germanium* | Ge | 71.93 | *Tantalum* | Ta | 181.45 |
| *Glucinum* | Gl | 9.01 | *Tellurium* | Te | 126.52 |
| Gold | Au | 195.74 | *Terbium* | Tr | 158.80 |
| *Helium* | He | (?) | *Thallium* | Tl | 202.61 |
| HYDROGEN | H | 1.00 | *Thorium* | Th | 230.87 |
| *Indium* | In | 112.99 | *Thulium* | Tm | 169.40 |
| Iodine | I | 125.89 | Tin | Sn | 118.15 |
| Iridium | Ir | 191.66 | Titanium | Ti | 47.79 |
| IRON | Fe | 55.60 | Tungsten | W | 183.43 |
| *Lanthanum* | La | 137.59 | Uranium | U | 237.77 |
| Lead | Pb | 205.36 | Vanadium | V | 50.99 |
| Lithium | Li | 6.97 | *Ytterbium* | Yb | 171.88 |
| MAGNESIUM | Mg | 24.10 | *Yttrium* | Y | 88.35 |
| Manganese | Mn | 54.57 | Zinc | Zn | 64.91 |
| Mercury | Hg | 198.49 | Zirconium | Zr | 89.72 |

The symbols of the elements represent not only the names but relative quantities. Thus O stands for 15.88 parts by weight of oxygen; N for 13.93 parts by weight of nitrogen; and hydrogen being that element which enters into combination in the smallest relative quantity, it is taken as the basis of the system, or H stands for 1 part by weight of hydrogen. What the symbol O really means then is that the quantity of matter represented by it is 15.88 times as great as the quantity of matter represented by the symbol H; and the quantity of matter represented by N is 13.93 times as great as that represented by the symbol H; and so on through the list. The figures do not represent absolute but relative masses. There are very serious difficulties encountered in determining the combining weights of the elements, and in regard to several given in the above table there is

considerable doubt as to the accuracy. Those of the elements with which we most frequently have to deal have, however, been determined with great care. Work in this field is being constantly carried on, and every year our knowledge in regard to the combining weights becomes more and more accurate.

**Symbols of Compounds.**—As the elements enter into combination in the proportion of their respective combining weights or simple multiples of these weights, it is an easy matter to represent the composition of compounds by means of the symbols. Thus hydrogen and chlorine combine in the proportion of their combining weights to form the compound hydrochloric acid. The compound is represented by the symbol HCl, which signifies that the compound contains hydrogen and chlorine in the proportion of 35.18 parts of chlorine to 1 part of hydrogen. So the symbol ZnO means a chemical compound consisting of 64.91 parts of zinc and 15.88 parts of oxygen; HCN means a compound made up of 1 part of hydrogen, 11.92 parts of carbon, and 13.93 of nitrogen. Whenever the symbols of the elements are placed side by side with no sign between them, as in the above examples, the resulting symbol means that the elements are in chemical combination. But, as has been pointed out, elements may combine in more than one proportion. In one of the two compounds of carbon and oxygen the elements are combined in the proportion of their combining weights, and the compound is represented by the symbol CO ; in the other compound the elements are combined in the proportion of twice the combining weight of oxygen to the combining weight of carbon, and the compound is represented by the symbol $CO_2$. The three compounds of iron and sulphur to which reference has already been made are represented by the symbols FeS, $Fe_2S_3$, and $FeS_2$. The first represents a compound in which the elements are combined in the proportion of their combining weights, or 55.60 parts iron to 31.83 parts sulphur ; the second represents a compound in which the elements are combined in the proportion of twice the combining weight of iron $(2 \times 55.60 = 111.20$

parts) to three times the combining weight of sulphur
($3 \times 31.83 = 95.49$ parts); and the third represents a com-
pound in which the elements are combined in the pro-
portion of the combining weight (55.60 parts) of iron to
twice the combining weight ($2 \times 31.83 = 63.66$ parts) of
sulphur. The four compounds of potassium, chlorine,
and oxygen above mentioned are represented by the sym-
bols $KClO$, $KClO_2$, $KClO_3$, and $KClO_4$, the meaning of
which will be clear from the explanation just given. By
means of such symbols all chemical compounds can be
represented, and they represent not only what elements
are contained in the compounds, but in what proportions
the elements are combined. They represent facts which
have been determined by experiment. Knowing the act-
ual weight of one constituent of any compound we can
calculate by the aid of the symbol the actual weights of
the other constituents and of the compound itself.
Thus, if we know the actual weight of the chlorine con-
tained in a quantity of potassium chlorate, $KClO_3$, we
can calculate how much potassium and how much oxygen
are contained in that same quantity, and also what the
quantity of potassium chlorate is. Suppose, for example,
we know that in a certain quantity of potassium chlorate
there is contained 25 grams of chlorine, and it is desired
to know how much potassium and how much oxygen
there are in this quantity, and also what the quantity of
potassium chlorate is. We know that the compound
$KClO_3$ is made up of 38.82 parts of potassium, 35.18
parts of chlorine, and 3 times 15.88, or 47.64, parts of
oxygen, the whole making 122.28 parts. The solution
of the following equations in proportion will give the
quantities desired :

$35.18 : 25 :: 38.82 :$ weight of potassium ;
$35.18 : 25 :: 47.64 :$ " " oxygen ;
$35.18 : 25 :: 121.64 :$ " " potassium chlorate.

**Chemical Equations.**—In dealing with cases of chemi-
cal action it is desirable to express by means of the
symbols which represent the elements and compounds
what takes place. In general, a chemical change is called

a chemical reaction, and these reactions are of three
kinds :

(1) Two or more elements or compounds may unite
directly to form one product.   This is called *combination.*
The following examples will suffice.  When mercury is kept
boiling in the air for a time it becomes covered with a layer
of a red substance which is a compound of mercury and
oxygen represented by the symbol $HgO$.   Magnesium
burns in the air and forms the compound $MgO$.   Hydro-
chloric acid, $HCl$, combines directly with ammonia, $NH_3$,
and forms the compound known as ammonium chloride,
$NH_4Cl$.   Water, $H_2O$, combines directly with lime or cal-
cium oxide, $CaO$, to form slaked lime or calcium hydrox-
ide, $CaO_2H_2$.   To represent these facts, the symbols of
the elements or compounds which act upon each other
are written with a plus sign between them, and the sign
of equality is written before the symbol of the product.
The chemical equations which represent the above-men-
tioned chemical reactions are :

$$Hg + O = HgO ;$$
$$Mg + O = MgO ;$$
$$HCl + NH_3 = NH_4Cl ;$$
$$H_2O + CaO = CaO_2H_2.$$

In reading the equations the plus sign is generally ren-
dered by *and*, and the sign of equality by *give*.   The first
equation should accordingly be read, " Mercury and oxy-
gen give mercuric oxide ;" but it represents besides this
fact the exact relations which exist between the quantities
of the elements and the compound which take part in the
reaction.

(2) The second kind of chemical reaction is *decomposi-
tion* or the opposite of combination.   Examples are fur-
nished by the decomposition of mercuric oxide into mer-
cury and oxygen by heat ; of potassium chlorate into
potassium chloride and oxygen by heat ; of water into
hydrogen and oxygen by the electric current ; and of cal-
cium carbonate or limestone, $CaCO_3$, into lime or calcium
oxide, $CaO$, and carbon dioxide, $CO_2$, by heat.   These re-
actions are represented by the following equations :

$$HgO \ \overset{\cdot}{=} \ Hg \ + O \ ;$$
$$KClO_3 = KCl + 3O \ ;$$
$$H_2O \ = 2H \ + O \ ;$$
$$CaCO_3 = CaO + CO_2.$$

The expressions 3O and 2H mean respectively three times the combining weight of oxygen and twice the combining weight of hydrogen, the figure being generally used in this way when the element is not in combination. It is, however, sometimes written the same as if the element were in combination, as will be explained later.

(3) The third kind of chemical reaction is that in which two or more compounds give rise to the formation of two or more others; or an element and a compound may act in such a way as to give another compound and another element. This is called *double decomposition* or *metathesis*. The following cases will serve as examples : Sulphuric acid, $H_2SO_4$, acts upon potassium nitrate, $KNO_3$, or saltpeter, forming potassium sulphate, $K_2SO_4$, and nitric acid, $HNO_3$; nitric acid, $HNO_3$, acts upon sodium carbonate, $Na_2CO_3$, forming sodium nitrate, $NaNO_3$, carbon dioxide, $CO_2$, and water, $H_2O$; hydrochloric acid, HCl, and zinc, Zn, give zinc chloride, $ZnCl_2$, and hydrogen. These facts are represented as below :

$$H_2SO_4 \ + 2KNO_3 = K_2SO_4 \ + 2HNO_3;$$
$$2HNO_3 + Na_2CO_3 = 2NaNO_3 + CO_2 + H_2O \ ;$$
$$2HCl \ + Zn \ = ZnCl_2 \ + 2H.$$

In the expressions $2KNO_3$, $2HNO_3$, $2NaNO_3$, and 2HCl, the large figures placed before the symbol of the compounds signify that the quantities of the compounds represented by the symbol are to be multiplied by the figure. Thus, HCl stands for $1 + 35.18 = 36.18$ parts of hydrochloric acid ; but 2HCl stands for $2(1 + 35.18) = 72.36$ parts ; 3HCl stands for $3(1 + 35.18) = 108.54$ parts ; etc.

**The Scope of Chemistry.**—A complete study of chemistry would involve the study of the action of all the elements upon one another under all possible circumstances, and a study of the action of all compounds upon one another and upon the elements under all cir-

cumstances. This indicates that the field is almost boundless; and if the facts were not related among one another, if every time a reaction is studied we are to expect something entirely different from all other reactions, the task would be practically hopeless. Fortunately a great many general facts are known, and reactions which at first seem to have no connection are by careful study shown to be related. Thus the study is very much simplified and made interesting. It must be our purpose to study the facts in as systematic a way as possible, and to be constantly on the alert to detect relations. The habit of comparing a new reaction with others already studied should be cultivated. In this way light will come out of the darkness, and the subject will gradually become clear. While the simplest way to begin the study of chemistry is by a consideration of the elements, the subject is complicated by the fact that we cannot readily obtain these elements without the aid of substances which have not been studied, and of processes which are incomprehensible. There are, however, two elements that occur in nature in enormous quantities, that can be obtained in the uncombined condition quite easily. As the kinds of action which they exhibit are of great importance and well calculated to give an insight into the nature of chemical action in general, we may profitably begin our study of chemical phenomena by a study of these two elements. They are oxygen and hydrogen. In learning the main facts in regard to these two elements we shall learn a great deal that will be of importance in enabling us to understand other chemical phenomena; we shall begin to learn how to study things chemically; and we shall thus prepare ourselves for a systematic study of the science of chemistry.

**Chemical Action accompanied by other kinds of Action.** —Whenever a chemical change takes place it is accompanied by other changes and, in order to gain a complete knowledge of the phenomenon, these other changes must be studied. Thus when sulphuric acid acts upon zinc the chemical change is represented both qualitatively and quantitatively by the equation

$$Zn + H_2SO_4 = ZnSO_4 + 2H.$$

In studying the reaction, the first thing to do is to learn the nature of the substances formed, and the relations between the substances which act upon each other and the products. This may be called the purely chemical study of the reaction. But much more can be learned in regard to it by careful observation. In the first place, we must take into account the fact that a solid and liquid here react to form a solid and a gas; and the question suggests itself, does this change to the gaseous condition exert any influence on the reaction, or is this a fact of no special importance? Again, it will be observed that accompanying the chemical change there is a marked rise in temperature, and we naturally inquire whether the quantity of heat evolved is definite for definite quantities of the substances, and, if so, what relation exists between them. There are still other changes which must be taken into account in order to get a complete knowledge of a chemical reaction, but, as yet, the study of the other changes has not been taken up in a general way, and our information in regard to them is comparatively limited. Within late years much progress has been made in the study of the heat changes which accompany chemical changes. It has been found that every chemical change gives rise either to an evolution or to an absorption of heat, and that for definite quantities of the same substances under the same circumstances the same amount of heat is evolved or absorbed. The special study of the heat changes connected with chemical changes is called *thermochemistry*. A consideration of the facts and laws of thermochemistry is of assistance in dealing with chemical reactions, and some attention will be paid to the subject in this book.

# CHAPTER II.

## A STUDY OF THE ELEMENT OXYGEN.

**Historical.**—The older chemists considered air to be a simple substance, but the experiments of Priestley (1774) and Scheele (1775) showed that the air contains two gases only one of which has the power to support combustion; and they succeeded independently of each other in showing that oxygen is a distinct substance. The discovery of oxygen had a very important bearing on the work of Lavoisier on combustion, and it was he who gave the name oxygen (or *oxygène*) to the gas, for the reason that he supposed it to be the essential constituent of all those chemical substances which are known as acids, the word being derived from the Greek οξυσ, acid, and γένειν, to produce. While this is generally true, it has since been found that there are other elements which have the power to give acid properties to the substances into the composition of which they enter, and, therefore, the name is misleading.

**Occurrence.**—Oxygen is the most widely distributed and most abundant element of the earth. It forms, as has been stated, about 47 per cent of the solid crust of the earth; eight-ninths of water; and about one-fifth of the air. It occurs also in combination with carbon and hydrogen, or with carbon, hydrogen, and nitrogen in the substances which go to make up the structure of living things, whether vegetable or animal. Besides this it forms a part of most manufactured chemical products.

**Preparation.**—Notwithstanding the abundant supply of oxygen in nature it is not a simple matter to get it in the free or uncombined state from most substances found in nature. As it forms eight-ninths of water, and water consists of only hydrogen and oxygen, the idea suggests itself at once that it may be made by the decomposition

of water. This can be accomplished without serious difficulty by means of an electric current, and both hydrogen and oxygen obtained in this way; but the method is expensive and more complicated than others which are available, and therefore it is not commonly used for the purpose. In the air the two gases nitrogen and oxygen are mixed together in the proportion of 1 volume of oxygen to 4 volumes of nitrogen. Here then, too, as in water, we have an enormous supply, but it is difficult to separate the oxygen from the nitrogen in such a way as to leave it uncombined. This can, however, be accomplished, and a method is now in practical use on the large scale for the purpose of preparing oxygen from the air. The method is based upon the fact that when barium oxide, BaO, is heated in a current of air it takes up oxygen and is converted into barium dioxide, $BaO_2$; and when the pressure upon the dioxide is sufficiently diminished, it is decomposed into the oxide, BaO, and oxygen, as represented in the equation

$$BaO_2 = BaO + O.$$

By this means the oxygen can be extracted from the air and obtained in the free condition.

Among substances which occur in nature and which can be used for the preparation of oxygen, manganese dioxide or pyrolusite, also called the black oxide of manganese, $MnO_2$, is the most important. It gives off a part of its oxygen when heated to a comparatively high temperature. It has been shown that the decomposition is represented by this equation:

$$3\ MnO_2 = Mn_3O_4 + 2O.$$

As will be seen, only one-third of the oxygen contained in the dioxide is thus obtained in the free state. A similar method is that used by Priestley when he discovered oxygen. It consists simply in heating mercuric oxide, HgO, when it is decomposed as represented thus:

$$HgO = Hg + O.$$

The substance potassium chlorate, $KClO_3$, is manufactured on the large scale for a variety of purposes and is,

therefore, easily obtained. It gives up its oxygen when heated. At first the decomposition represented by this equation takes place:

$$8KClO_3 = 5KClO_4 + 3KCl + 4O.$$

The products are potassium perchlorate, $KClO_4$, potassium chloride, $KCl$, and oxygen, one-sixth of the total oxygen being given off in the first stage. This part of the decomposition takes place readily, and at a comparatively low temperature. If, after it is complete, the temperature is raised considerably higher, more gas is given off and the change represented by the equation

$$KClO_4 = KCl + 4O$$

is accomplished. The final result is, therefore, the setting free of all the oxygen contained in the chlorate. This fact is represented thus:

$$KClO_3 = KCl + 3O.$$

The best method for use in the laboratory for the preparation of oxygen consists in heating a mixture of equal parts of coarsely powdered manganese dioxide and potassium chlorate. This mixture gives up oxygen very readily under the influence of heat. Potassium chlorate alone requires to be heated to a temperature of over 350° C. to effect its decomposition, but when mixed with manganese dioxide the decomposition takes place at about 200° C. The manganese dioxide does not lose any of its oxygen under the circumstances. Other substances, such as ferric oxide, copper oxide, etc., may be used with similar effect. No satisfactory explanation of the action of these substances has been given. Recent experiments have shown that, when manganese dioxide is used, oxygen, chlorine, and potassium permanganate, $KMnO_4$, are first formed. The permanganate is decomposed by heat, yielding the manganate, $K_2MnO_4$, the dioxide, and oxygen; and, finally, the manganate is decomposed by chlorine, yielding potassium chloride, the dioxide, and oxygen.

**Physical Properties.**—Oxygen is a colorless, tasteless, inodorous gas. It is only slightly soluble in water, 100

volumes of water at 0° dissolving 4.1 volumes of oxygen. It is slightly heavier than air, its specific gravity is 1.10563, and 1 liter under 760 mm. pressure and at temperature 0° weighs 1.429 grams, while a liter of air weighs 1.2932 grams. In dealing with chemical elements and compounds which are gaseous, it is customary to use hydrogen instead of the air as the standard for specific gravity. While the specific gravity of oxygen in terms of air is 1.10563, in terms of hydrogen it is 15.88, or, in other words, a given volume of oxygen weighs 15.88 as much as the same volume of hydrogen under the same conditions. Under a pressure of 50 atmospheres and at a temperature − 118° it is condensed to a liquid of specific gravity 0.978. Liquid oxygen is a pale steel-blue transparent and very mobile liquid which boils at −181°.4 at ordinary pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen to a white solid.

**Chemical Properties.**—At ordinary temperatures oxygen does not act readily upon most other things, as can be clearly shown by putting a variety of substances in the gas without heating them. If they are left for a considerable time some evidence of change will be observed, but generally the change is extremely slow unless the temperature is raised. At higher temperatures, different for different substances, it combines with all the elements except fluorine, and it acts readily upon a large number of compounds. Its action is generally accompanied by an evolution of heat and light, and the process under these circumstances is called combustion. This action may be illustrated by first heating and then introducing into vessels containing oxygen, sulphur, charcoal, iron in the shape of a steel watch-spring, and a bit of phosphorus. The phenomena observed show that chemical action takes place, but they do not show what is formed. It is evident that in each case light and heat are evolved, and that the substances introduced into the oxygen are changed to other things. In the case of phosphorus the light given off is very intense, while in that of carbon and that of sulphur it is only slight. In

the vessel in which the burning of the iron takes place a reddish-brown substance is deposited, while in that in which the phosphorus is burned dense white fumes are formed and at first the product is partly deposited upon the walls of the vessel in the form of a white powder that looks like snow. After standing for some time over water it disappears and the water evidently contains something in solution. A thorough study of the reactions above mentioned has shown that they consist in the chemical combination of oxygen with the substances burned. The light and heat are results of the chemical action. The reactions are represented by the following equations:

$$\text{With sulphur,} \qquad S + 2O = SO_2;$$
$$\text{`` carbon,} \qquad C + 2O = CO_2;$$
$$\text{`` iron,} \qquad 3Fe + 4O = Fe_3O_4;$$
$$\text{`` phosphorus,} \ 2P + 5O = P_2O_5.$$

The products are sulphur dioxide, $SO_2$, a colorless pungent gas; carbon dioxide, $CO_2$, a colorless gas; magnetic oxide of iron, $Fe_3O_4$, a reddish-brown substance; and phosphorus pentoxide, $P_2O_5$, a white solid which dissolves in water.

**Burning in the Air and Burning in Oxygen.**—One cannot well help noticing a strong resemblance between the burning of substances in the air and in oxygen; and the question naturally suggests itself, Are these two acts the same in character, or is there a difference between them? To answer this question, we must burn the same substances in pure oxygen and in air, and determine whether the same products are formed in the two cases, and at the same time whether anything else is formed. If we should make this comparison in any case, we should find that, whether a substance burns in the air or in pure oxygen, the same product is formed, and nothing else. It is therefore certain that the act of burning in the air is due to the presence of oxygen. But substances do not burn as readily in the air as in oxygen, and some which burn in oxygen do not burn in the air. This is

due to the fact that only about one-fifth of the volume of the air is oxygen, while most of the remaining four-fifths consists of an extremely inactive element, nitrogen, which takes no part in the process of burning.

**Phlogiston Theory.**—Fire in its various forms is one of the longest known chemical phenomena. From the earliest times it has attracted the attention of men and has been the subject of speculative and experimental study. It was one of the elementary substances of Aristotle, as has already been stated. The first comprehensive theory covering all cases of combustion was that put forward by Stahl and known as the *phlogiston theory*. According to this, every combustible substance contains something, called phlogiston, which escapes in the process of burning. It was repeatedly pointed out that some substances grow heavier by burning, or rather that the products of combustion weigh more than the substance burned.

This can be shown to be true in the case of zinc by placing some turnings of the metal on one pan of a balance and determining the weight. If now the metal is burned it will change almost completely to a white powder, and this will weigh more than the zinc.

If an ordinary candle is placed on one pan of a balance and a glass vessel open at both ends and filled with large pieces of sodium hydroxide or caustic soda is suspended directly over the candle in such way that the smoke from the candle must pass upwards through the tube, and a similar tube is suspended over the other pan of the balance, and equilibrium is then established, it will be found that the pan on which the candle is placed will gradually grow heavier and sink as the candle burns away. The explanation of this is simply that the gases which are formed by the burning of the candle are retained by the caustic soda, and they weigh more than the candle from which they were formed by combustion.

Facts like those mentioned were known when the phlogiston theory was held, but they do not appear to have made a very strong impression upon chemists. Chemists were at all events not able to give a satisfactory explanation. This remained for Lavoisier.

**Lavoisier's Explanation of Combustion.**—When Lavoisier began his work oxygen was unknown, but it was discovered soon afterward ; and this discovery was of the highest importance for the explanation of the phenomenon of combustion. Lavoisier showed that when a substance is burned in oxygen or in the air, some of the gas is used up. He then weighed the substance burned, the oxygen used up, and the product formed, and found that this relation holds good :

$$\text{Weight of Substance burned} + \text{Weight of Oxygen used up} = \text{Weight of Product formed.}$$

Having established this relation in a number of cases, it followed that the process of combustion consists in the chemical combination of oxygen with the substance burned. There was no longer room for the hypothetical phlogiston, and since that time it has not occupied a place in the thoughts of most chemists.

**Combustion.**—By the term combustion in its broadest sense is meant any chemical act which is accompanied by an evolution of light and heat. Ordinarily, however, it is restricted to the union of substances with oxygen, as this union takes place in the air, with evolution of light and heat. Substances which have the power to unite with oxygen are said to be *combustible*, and substances which have not this power are said to be *incombustible*. Most elements combine with oxygen under proper conditions, and are therefore combustible. Most compounds formed by the union of oxygen with combustible substances are incombustible. For example, the sulphur dioxide, carbon dioxide, magnetic oxide of iron, and phosphorus pentoxide, formed when sulphur, carbon, iron, and phosphorus are burned in oxygen, are incombustible. They contain oxygen and they cannot combine directly with more.

**Kindling Temperature.**—We have seen that substances do not usually combine with oxygen at ordinary temperatures, but that in order to effect the union the temperature must be raised. If this were not the case, it is plain that every combustible substance in nature would burn up,

for the air probably supplies a sufficient quantity of oxygen for this purpose. Some substances need to be heated to a high temperature before they will combine with oxygen; others require to be heated but little. If we were to subject pieces of phosphorus, of sulphur, and of carbon to the same gradual rise in temperature, we should find that the phosphorus takes fire very easily, only a slight elevation of temperature being necessary; next in order would come the sulphur; and last the carbon. If we were to repeat these experiments a number of times, we should find that the phosphorus always takes fire at the same temperature, and a similar result would be reached in the case of sulphur and carbon. Every combustible substance has its *kindling temperature;* that is, the temperature at which it will combine with oxygen. Below this temperature it will not combine with oxygen. If a piece of wood should be heated to its kindling temperature all at once, it would burn up as rapidly as it could secure the necessary oxygen; but the burning does not usually take place rapidly, for the reason that only a small part of it is at any one time heated to the kindling temperature. Watch a stick of wood burning, and see how, as we say, "the fire creeps" slowly along it. The reason of the slow advance is simply this: Only those parts of the stick which are nearest the burning part become heated to the kindling temperature. They take fire and heat the parts nearest them, and so on gradually throughout the length of the stick.

**Slow Oxidation.**—Substances may combine slowly with oxygen without evolution of light. Thus, if a piece of iron is allowed to lie in moist air, it becomes covered with rust. The rust is similar to the substance formed when iron is burned in oxygen. Both are formed by the union of iron and oxygen. Magnesium burns in the air and forms a white compound containing oxygen. It burns with increased brilliancy in oxygen, forming the same compound. If left in moist air for some days or weeks, it becomes covered with a layer of the same white substance. If this is scraped off, and the magnesium again allowed to lie, it will again become covered

with a layer of the compound with oxygen, and this may be continued until the magnesium has been completely converted into the same substance that is formed when it burns in oxygen or in the air. Many other cases of slow oxidation might be described, some of which, such as the decay of wood, are constantly taking place. The most important illustration of slow oxidation is that which takes place in our bodies, for, as we shall see, the food of which we partake undergoes a great many changes, some of the substances uniting with oxygen, and thus keeping up the temperature of our bodies. This, however, is done without evolution of light. We take large quantities of oxygen into our lungs in the act of breathing. This acts upon various substances presented to it, oxidizing them to other forms which can easily be got rid of. More will be said in regard to the breathing process of animals and plants when the subject of carbon and its compounds is taken up.

**Heat of Combustion.**—What is the chief difference between combustion, as we ordinarily understand it, and slow oxidation? As far as can be judged by a cursory examination, it is that in the former there is an evolution of light and much heat, while in the latter there is apparently but little heat evolved and no light. Remembering that the reason why a body gives light is that it is heated to a sufficiently high temperature, the problem resolves itself into a question of heat. What difference, if any, is there between the quantity of heat given off when a substance burns, and when it undergoes slow oxidation without evolution of light? Experiment has shown that *there is no difference.* In one case all the heat is given off in a short space of time, and therefore the temperature of the substance becomes high and it emits light. In the other the heat is given off slowly and continues for a much longer time, and therefore the temperature of the substance does not get high, as surrounding substances conduct off the heat nearly as rapidly as it is evolved. If, however, we were to measure the *quantity* of the heat, we should find it to be the same in both cases.

We can measure the heat given off or absorbed in a chemical reaction by allowing the reaction to take place in a vessel called a calorimeter, so constructed as to prevent loss of heat, and containing a known weight of water. The temperature of the water is noted at the beginning of the operation and at the end. A quantity of heat is generally stated by giving the number of grams of water which it will raise one degree (Centigrade) in temperature. The quantity of heat necessary to raise a gram of water one degree in temperature is the unit used in heat measurements. It is called the *calorie*. If we say that the quantity of heat evolved in any reaction is 250 calories (written generally 250 cal.), this means simply a quantity of heat capable of raising the temperature of 250 grams of water one degree or of one gram of water 250 degrees in temperature. Sometimes it is convenient to use a larger unit. The quantity of heat required to raise the temperature of one kilogram of water one degree serves the purpose. This is the large calorie. To distinguish it from the smaller one it is written with a capital. Thus, 250 Cal. means 250 large calories. The large calorie is obviously 1000 times greater than the small calorie.

To repeat, then: by the heat of combustion of a substance is meant simply the quantity of heat given off when a certain weight of the substance combines with oxygen. In order to avoid confusion it is necessary to have an agreement in regard to the weight of substance which shall be used as the standard. This may be a gram or any other weight, but for the purposes of chemistry it is most convenient to take weights in proportion to the combining or atomic weights. Thus, by the heat of combustion of carbon is meant the quantity of heat evolved by the combination of 11.92 grams of carbon with $2 \times 15.88 = 31.76$ grams of oxygen. By the heat of combustion of sulphur is meant the quantity of heat evolved in the combination of 31.83 grams sulphur with $2 \times 15.88 = 31.76$ grams oxygen, etc.

Not only is the heat of combustion the same whether

the union with oxygen takes place slowly or rapidly, but the heat evolved in any given chemical reaction is always the same, and chemical action is always accompanied by an evolution or absorption of heat.

**Heat of Decomposition.**—Just as it is true that a definite quantity of heat is evolved when two or more elements combine chemically, so also it is true that in order to overcome the force which holds these elements together the same quantity of heat is absorbed. Thus, the heat of formation of mercuric oxide, HgO, is 30,660 cal.; or, in other words, when 198.49 grams of metallic mercury and 15.88 grams of oxygen combine, 30,660 calories of heat are evolved. Now, we have seen that when heat is applied to the compound it is decomposed into its elements. To effect this decomposition, as much heat is absorbed as was evolved in the formation of the compound.

**Chemical Energy and Chemical Work.**—Any substance which has the power to unite with others can do *chemical work :* it possesses *chemical energy.* Thus, all combustible substances can do work. In uniting with oxygen heat is evolved, and this can be transformed into motion. In the case of the steam-engine, the cause of the motion is the burning of the fuel, which is a chemical act. We thus see that the source of the power of the steam-engine is chemical energy. Substances, on the other hand, which have no power to combine with others have no power to do chemical work, or they have no chemical energy. So far as power to combine with oxygen is concerned, water is a substance of this kind, as is also carbon dioxide, the gas formed when carbon is burned in oxygen. In order that they may do work by combining with oxygen, they must first be decomposed, and their constituents put together in some form in which they have the power of combination. This decomposition of carbon dioxide and water is taking place constantly on the earth. All plant-life is dependent on it. The products of the action, i.e., the different kinds of wood, have chemical energy,—they can do chemical work. This power to do work has been acquired from the heat

of the sun, which is the main force used in decomposing the carbon dioxide and water. We have thus a transformation of the sun's heat into chemical energy, which is stored up in the combustible woods. The quantity of heat which is given off in burning wood is believed to be exactly equal to the quantity of heat used up in its formation.

**Oxides.**—The compounds of oxygen with other elements are called *oxides*. To distinguish between different oxides, the name of the element with which the oxygen is in combination is prefixed. Thus, the compound of zinc and oxygen is called *zinc oxide;* that of calcium and oxygen, *calcium oxide;* that of silver and oxygen, *silver oxide;* etc. When an element forms more than one compound with oxygen, suffixes are used to distinguish between them. Thus in the case of copper there are two oxides which have the composition represented by the symbols $Cu_2O$ and $CuO$. The former is known as *cuprous oxide* and the latter as *cupric oxide*. That oxide which contains the smaller quantity of oxygen in combination with a given quantity of the other element is designated by the suffix *ous;* that which contains the larger proportion of oxygen is designated by the suffix *ic*. In other cases the number of combining weights of oxygen contained in the compound is indicated by the name. Thus, *manganese dioxide* is $MnO_2$; *sulphur trioxide* is $SO_3$; etc.

# CHAPTER III.

## A STUDY OF THE ELEMENT HYDROGEN.

**Historical.**—Hydrogen was discovered as a distinct substance by Cavendish in 1766, although it had been observed as an inflammable gas before that time.

**Occurrence.**—It occurs to some extent in the free condition, and issues from the earth in small quantity in some localities. It is, for example, a constituent of the gases which escape from the petroleum wells in Pennsylvania. It has also been shown to occur in enormous quantities in the atmosphere of the sun. On the earth it occurs chiefly, however, in combination in water, of which it forms 11.11 per cent. It occurs also in most substances of animal and vegetable origin, such as the various kinds of wood and fruits, and the tissues of all animals. In these products of life it is contained in combination with carbon and oxygen or with carbon, oxygen, and nitrogen.

**Preparation.**—The simplest way, theoretically, to prepare hydrogen is by the decomposition of water by the electric current. It has already been stated that when an electric current is passed through water the two gases oxygen and hydrogen are liberated. But this method is less convenient and more expensive than other methods which are available, and it is therefore used only under special circumstances. It is particularly well adapted to the preparation of small quantities of pure hydrogen.

Some elements when brought in contact with water at the ordinary temperature decompose it and set hydrogen free. The two most easily obtained elements which act in this way are sodium and potassium. If a small piece of potassium is thrown upon water, a flame is observed at once. If sodium is used, it is seen to form a small

ball which moves about on the surface of the water with a hissing sound, but under ordinary circumstances no flame is observed. By applying a flame to the ball something takes fire and burns. By filling a good-sized test-tube with water and inverting it in a larger vessel and bringing a small piece of sodium wrapped in a piece of filter-paper below the mouth of the tube, the sodium will rise to the top of the tube when released, and it will then be seen that a gas is evolved which gradually depresses the water in the tube. A similar experiment with potassium gives a similar result. The gas given off in each case is hydrogen. By evaporating off the water left in the vessel there will be found in each case a white substance of marked chemical properties. That formed with the potassium is known as potassium hydroxide, or caustic potash, and has the composition represented by the symbol KOH; that formed with the sodium is known as sodium hydroxide, or caustic soda, and is represented by the symbol NaOH. The reactions which take place between potassium and sodium and water are represented by the equations

$$K + H_2O = KOH + H; \text{ and}$$
$$Na + H_2O = NaOH + H.$$

Half the hydrogen of the water which is decomposed is replaced by the potassium or the sodium, as the case may be. These reactions are partly described by saying that the potassium or sodium is *substituted* for half the hydrogen in the water, and the act is called *substitution*. This is a very common kind of chemical action, and we shall constantly meet with it in the course of our study. The reaction is one of double decomposition or metathesis, two substances acting upon each other to form two others. The cause of such a reaction is to be sought for in the different degrees of attraction exerted by the elements upon one another. In general terms, if two compounds *AB* and *CD* are brought together, and the element *A* has for *C* a stronger attraction than *A* for *B*, and *B* has for *D* a stronger attraction than it has for

*A*, then reaction will take place, to some extent at least, according to the equation

$$AB + CD = AC + BD.$$

The action may be modified by a number of circumstances which will be treated of in due time. It is evident, however, now that a very important problem for the chemist to solve is the determination of the attraction which the elements exert upon one another. It is extremely difficult to make these determinations, but something can be learned in regard to them by a study of the changes in temperature which accompany them. The attraction is not proportional to the heat evolved, for reasons which will be pointed out later, but there is some relation between them.

Some substances which decompose water slowly at the ordinary temperature do so readily at a higher temperature. This is true, for example, of iron. At ordinary temperatures it decomposes water, as is seen in the formation of a coating upon it when left in contact with water. At higher temperatures when the iron is red-hot it decomposes water very readily, and hydrogen may be made in quantity by this means. In the laboratory the iron may be heated in a gun-barrel or in a porcelain tube. When steam is passed over it the decomposition represented in this equation takes place :

$$3Fe + 4H_2O = Fe_3O_4 + 8H.$$

The iron combines with the oxygen and liberates the hydrogen.

Carbon, in the form of charcoal or coal, may be used in a similar way to effect the decomposition of water and the liberation of hydrogen. At a high heat the reaction takes place mainly as represented thus :

$$C + H_2O = CO + 2H.$$

A mixture of two gases, carbon monoxide and hydrogen, is thus formed. This mixture is the essential part of the gas which has of late years come into such extensive

use under the name " water-gas." This is formed by passing steam over highly heated anthracite coal.

By far the most convenient method for making hydrogen consists in treating a metal with an acid. Among the metals best adapted to the purpose are zinc and iron, and indeed zinc is almost exclusively used. As will be seen later, acids are substances that contain hydrogen, and are characterized by the property that they give up this hydrogen very easily and take up other elements in the place of it. Among the common acids found in every laboratory are *hydrochloric acid, sulphuric acid,* and *nitric acid.* The chemistry of these compounds will be treated of in due time ; but, as we shall be obliged to use them before they are taken up systematically, a few words in regard to them are desirable in this place.

*Hydrochloric acid* is a compound of hydrogen and chlorine. It is a gas which dissolves easily in water. It is this solution which is used in the laboratory, and which is manufactured in enormous quantities in connection with the manufacture of soda or sodium carbonate. Its chemical symbol is HCl. In commerce it is not uncommonly called " muriatic acid."

*Sulphuric acid* is a compound of sulphur, oxygen, and hydrogen in the proportions represented by the formula $H_2SO_4$. It is an oily liquid and is frequently called " oil of vitriol." It is manufactured in very large quantities, as it plays an important part in many of the most important chemical industries.

*Nitric acid* is a compound containing nitrogen, oxygen, and hydrogen in the proportions represented by the formula $HNO_3$. It is a colorless liquid, though, as we get it, it is commonly colored straw-yellow.

When a metal, such as zinc, is brought in contact with hydrochloric or sulphuric acid, an evolution of hydrogen takes place at once. The reactions are as represented in these equations :

$$Zn + 2HCl = ZnCl_2 + 2H ;$$
$$Zn + H_2SO_4 = ZnSO_4 + 2H.$$

Each combining weight of zinc liberates and replaces two combining weights of hydrogen.

The action between iron and these two acids is of the same character :

$$Fe + 2HCl = FeCl_2 + 2H;$$
$$Fe + H_2SO_4 = FeSO_4 + 2H.$$

The hydrogen obtained from acids by the action of metals is not pure, but it can be purified by treatment with appropriate substances. That obtained by the decomposition of water by the electric current is pure.

**Physical Properties.**—Hydrogen is a colorless, inodorous, tasteless gas. That made by the action of acids on zinc or iron has a somewhat disagreeable odor which is due to the presence of other gases in small quantity. It is not poisonous, and may therefore be inhaled with impunity. We could not, however, live in an atmosphere of hydrogen, as we need oxygen. It is the lightest known substance. Its specific gravity in terms of the air standard is 0.06926. A litre under 760 mm. pressure and at 0° weighs 0.089873 gram. Under Oxygen it was stated that in chemistry hydrogen is commonly taken as the standard of specific gravity, and that, hydrogen being unity, the specific gravity of oxygen is 15.88. The gas is only slightly soluble in water. 100 volumes of water take up 1.93 volumes of hydrogen. The fact that hydrogen is lighter than the air is shown by opening a vessel which contains it and turning the mouth of the vessel upward. The gas escapes at once, and in a very short time no evidence of its presence can be obtained. Light vessels as, for example, soap-bubbles or collodion-balloons filled with the gas rise in the air, and it is used for the purpose of filling large balloons.

Hydrogen has been converted into the liquid form under a pressure of 20 atmospheres at a temperature of − 234°.5. Its boiling-point under ordinary atmospheric pressure is − 243°.5.

Hydrogen passes readily through porous substances, or it diffuses rapidly. This can easily be demonstrated in the case of porous earthenware and paper. It

also passes readily through some metals, as iron and platinum, when heated to redness. There is a direct relation between the specific gravity of gases and the rate at which they diffuse. The lower the specific gravity the more rapid the diffusion. The law governing these phenomena is :

*The rate of diffusion of gases is approximately inversely proportional to the square roots of their specific gravities.*

The specific gravity of hydrogen being 1 and that of oxygen nearly 16 (15.88), the rate of diffusion of oxygen is approximately $\frac{1}{4}$ that of hydrogen. If hydrogen is on one side of a porous wall, and oxygen on the other, the hydrogen will pass through the wall so much more rapidly than the oxygen that there will be an accumulation of hydrogen on one side of the wall, and if the vessel were closed there would be increased pressure on that side. The ready passage of gases through porous walls is a matter of great importance in connection with the ventilation of dwellings. Most of the materials used in building are porous and permit the passage of gases through them in both directions, and change of air is secured in this way to some extent.

**Chemical Properties.**—Under ordinary circumstances, hydrogen is not a particularly active element. It does not unite with oxygen gas at ordinary temperatures, but, like other combustible substances, it must be heated up to the kindling temperature before it will burn. If a lighted match is applied to it, it takes fire at once. The flame is colorless or slightly blue. Generally the flame is somewhat colored in consequence of the presence of foreign substances; but that it is colorless when the gas is burned alone can be shown by burning it as it issues from a platinum tube which is itself not chemically acted upon by the heat. Although the flame is not luminous it is intensely hot, as can be seen by inserting into it a coil of platinum wire, which will at once become red-hot and emit light accordingly.

The burning of hydrogen in the air, like the burning of other combustible substances in the air, consists in a

union of the gas with oxygen. This has been shown to be true by most elaborate experiments on the combustion of hydrogen in oxygen and in the air. On the other hand, substances which burn in the air are extinguished when put in a vessel containing hydrogen. This is equivalent to saying that a substance which is uniting with oxygen does not continue to unite with oxygen when put in an atmosphere of hydrogen, and does not combine with hydrogen. The fact is expressed by saying that hydrogen does not support combustion. This can be shown by holding a vessel filled with hydrogen with the mouth downward, and inserting into it a lighted taper supported on a wire. The gas takes fire at the mouth of the vessel, but the taper is extinguished.

Ordinarily we say that hydrogen burns in oxygen, but, as the act consists in the union of the two gases, it would seem probable that oxygen will burn in an atmosphere of hydrogen. This can be shown to be true by a proper arrangement of apparatus. If we were surrounded by an atmosphere of hydrogen we should probably speak of oxygen as a combustible gas in the same way that we now speak of hydrogen as a combustible gas.

It can easily be shown that, when hydrogen is burned either in oxygen or air, water is formed. The simplest way to show this is by holding a glass plate or some other incombustible object a short distance above a flame of hydrogen. It will be seen that drops of water are condensed upon it.

Hydrogen combines with many other elements besides oxygen, and forms some of the most important and interesting compounds, such as hydrochloric acid, $HCl$; sulphuretted hydrogen or hydrogen sulphide, $H_2S$; ammonia, $NH_3$; marsh gas, $CH_4$; and all the acids. On account of its affinity for oxygen it is used very extensively in the laboratory for the purpose of extracting oxygen from compounds containing it. Thus, when hydrogen is passed over heated copper oxide, $CuO$, it combines with the oxygen to form water, and the copper

is left in the free or uncombined state. The reaction is represented thus :

$$CuO + 2H = H_2O + Cu.$$

A similar reaction takes place when hydrogen is passed over highly heated oxide of iron, $Fe_2O_3$ :

$$Fe_2O_3 + 6H = 2Fe + 3H_2O.$$

The removal of oxygen from a compound is called *reduction*. Reduction is therefore plainly the opposite of oxidation. Any substance which has the power to abstract oxygen is spoken of as a *reducing agent*, just as any substance which has the power to add oxygen to a substance, or to decompose it by the action of oxygen, is called an *oxidizing agent*.

A number of metals have the power to absorb a large quantity of hydrogen when they are heated to red heat in the gas. This phenomenon is shown most strikingly by palladium, which under the most favorable conditions takes up something more than 935 times its own volume of hydrogen. The gas is given up at elevated temperature in a vacuum. When it absorbs hydrogen, palladium undergoes marked changes in properties. Its volume is increased, and its magnetic and electric properties are also changed. It was suggested by Graham, who first observed this phenomenon, that the hydrogen held in combination by the palladium is something quite different from ordinary hydrogen, and that it must have some properties like those of the so-called metals. He therefore called the combined hydrogen *hydrogenium*.

**Comparison of Oxygen and Hydrogen.**—Hydrogen and oxygen are different kinds of matter, just as heat and electricity are different kinds of energy. Heat can be converted into electrical energy, and electrical energy into heat, but one element cannot by any means known to us be converted into another. They are apparently entirely independent of each other. The question will therefore suggest itself, whether, in spite of their ap-

parent independence, there is not some relation be-
tween the different elements which reveals itself by
similarity in properties?  It will be found that the ele-
ments can be separated into groups or families accord-
ing to their properties.  There are some elements, for
example, which in their chemical conduct resemble oxy-
gen markedly.  These elements constitute the *oxygen
family*.  So far as hydrogen is concerned, however, it
stands by itself.  There is no other element which con-
ducts itself like it.  If we compare it with oxygen, we
find very few facts which indicate any analogy between
the two elements.  In their physical properties they
are, to be sure, similar.  Both are colorless, inodorous,
tasteless gases.  On the other hand, oxygen combines
readily with a large number of substances with which
hydrogen does not combine.  Oxygen, as we have seen,
combines easily with carbon, sulphur, phosphorus, and
iron.  It is a difficult matter to get any of these elements
to combine directly with hydrogen.  Further than this,
substances which combine readily with hydrogen do not
combine readily with oxygen.  The two elements ex-
hibit opposite chemical properties.  What one can do
the other cannot do.  This oppositeness of properties is
favorable to combination ; for not only do hydrogen and
oxygen combine with great ease under proper condi-
tions, but, as we shall see later, it is a general rule that
elements of like properties do not readily combine with
one another, while elements of unlike properties do
readily combine.

# CHAPTER IV.

**Burning of Hydrogen.**—Attention has already been called to the fact that, when hydrogen burns, water is formed. It is now necessary that this reaction should be studied more thoroughly with the view of discovering, as far as possible, exactly what takes place. One of the first questions to be answered is what relation exists between the weights of the hydrogen burned, the oxygen used up in the burning process, and the water formed? But to weigh gases accurately and to collect small quantities of water and weigh it are by no means simple operations, and a great deal of work has been done upon the problem under consideration. No good method has been devised for the quantitative study of the combination of hydrogen and oxygen by ordinary combustion. On the other hand, very accurate experiments on the subject have been made in three other ways, a brief account of which will now be given.

**Method of Dumas.**—The first accurate experiments on the combustion of hydrogen are those of Dumas. The method employed by this chemist was as follows: He passed carefully purified hydrogen over heated copper oxide and collected the water formed. The reaction involved is that represented by the equation

$$CuO + 2H = H_2O + Cu.$$

The weight of the oxygen that entered into combination with hydrogen was obtained by weighing the vessel containing the copper oxide before and after the experiment. The loss in weight represented the weight of the oxygen which had been abstracted. The water was collected by passing the gases formed through an empty glass vessel in which most of the water was condensed, and then through tubes containing molten caustic potash and phosphorus pentoxide, substances which

have a marked power to absorb water and hold it in combination. In nineteen experiments he obtained a total amount of water weighing 945.439 grams, and the total amount of oxygen used in the formation of this amount of oxygen used in the formation of this amount of oxygen was 840.161 grams. According to these results the ratio between hydrogen and oxygen in water expressed in percentages is:

$$
\begin{array}{ll}
\text{Oxygen} & 88.864 \\
\text{Hydrogen} & 11.136 \\
\hline
& 100.000
\end{array}
$$

Morley with great pains proceeded as follows: He weighed comparatively large volumes of oxygen in the form of gas; he then weighed hydrogen after it had been absorbed by palladium. The hydrogen being expelled from the palladium, it was brought together with the oxygen, with which it was caused to combine by means of electric sparks. The water thus formed was carefully collected and weighed. Twelve experiments gave results that agreed closely with one another. The mean of these shows that hydrogen and oxygen combine in the ratio of 1 part of hydrogen to 15.8792 parts of oxygen. Dumas' result expressed in the same way is 1 : 15.961.

**Eudiometric Method.**—When hydrogen and oxygen are mixed at ordinary temperatures no chemical change takes place, and the two gases may be left in contact with each other indefinitely without chemical action. If, however, a spark is brought in contact with the mixture violent action takes place, accompanied by a flame and explosion. The action consists in the sudden combination of the two gases to form water. It may be illustrated in a number of ways: most simply by filling soap-bubbles with the mixture of the two gases and applying a flame to them. The explosion which ensues is harmless. Plainly, to study the combination of hydrogen and oxygen by exploding a mixture of the gases will require special precautions. It can be carried out by the aid of the *eudiometer* (from εὐδία, good air, and μέτρον, a measure, an instrument for determin-

ing the purity of air). The eudiometer is simply a tube graduated in millimeters and having two small platinum wires passed through it at the closed end, nearly meeting inside and ending in loops outside, as shown in Fig. 1. The eudiometer is filled with mercury, inverted in a mercury trough, and held in an upright position by means of proper clamps. For the purpose of the experiment a quantity of hydrogen is passed up into the tube, and its volume accurately measured. About half this volume of oxygen is then introduced and the volume again accurately determined, and after the mixture has been allowed to stand for a few minutes a spark is passed between the wires in the eudiometer by connecting the loops with the poles
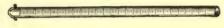
FIG. 1.

of a small induction coil or with a Leyden jar. Under these circumstances the explosion takes place noiselessly and with little or no danger. If the interior of the tube was dry before the explosion, it will be seen to be moist afterwards, and a marked decrease in the volume of the gases is also observed. That water is the product of the action has been proved beyond any possibility of a doubt, over and over again. As the liquid water which is formed occupies an almost inappreciable volume as compared with the volume of the gases which combine, the decrease in volume represents the total volume of hydrogen and oxygen which have combined. Now, if the experiment is performed with the two gases in different proportions, it will be found that only when they are mixed in the proportion of 2 volumes of hydrogen to 1 volume of oxygen do they completely disappear in the explosion. If there is a larger proportion of hydrogen present, the excess is left over; and the same is true of the oxygen. It will thus be seen that when hydrogen and oxygen combine to form water, they do so in the proportion of 2 volumes of hydrogen to 1 volume of oxygen or more accurately 2.0008 to 1.

**Calculation of the Results Obtained in Exploding Mixtures of Hydrogen and Oxygen.**—Having determined that whenever hydrogen and oxygen combine, they do so in the proportion 1 volume oxygen to 2 volumes hydrogen, and that when they combine the volume of liquid water formed measures so little as to amount to nothing in the measurements, we know that whenever a mixture of hydrogen and oxygen is exploded, no matter in what proportions they may be present, the volume of gas which disappears as such consisted of 2 volumes of hydrogen and 1 volume of oxygen, or, in other words, one-third of the volume which disappears was oxygen and two-thirds hydrogen. Take this example: A quantity of hydrogen corresponding to 60 cc. under standard conditions is introduced into a eudiometer; 40 cc. of oxygen are added. What contraction will there be on exploding the mixture? Plainly the 60 cc. of hydrogen will combine with 30 cc. of oxygen. The 90 cc. of gas will disappear, and 10 cc. of oxygen will remain uncombined. From a total volume of 100 cc., therefore, we get a contraction to 10 cc. One-third of the contraction represents the oxygen and two-thirds the hydrogen.

**Determination of the Volume of Water Vapor formed by Union of Definite Volumes of Hydrogen and Oxygen.** —The experiments which have been described enable us to draw the conclusion that hydrogen and oxygen combine in certain proportions by volume and by weight, and that a definite weight of water is formed; further, that the volume of liquid water formed when the two gases combine is inappreciable as compared with that of the gases. The question remains to be answered, what relation exists between the volumes of the combining gases and that of the water in the form of vapor? This can be determined by causing the gases to combine in a eudiometer at a temperature sufficiently high to keep the water in the form of vapor. The simplest arrangement for accomplishing this is that shown in Fig. 2. A long eudiometer, the upper half of which is divided into three equal divisions marked on the outside, is filled with mercury and inverted in a bath of mercury. It is

then surrounded by a large tube or jacket arranged as shown in Fig. 2. This is connected through the cork at the lower end with a vessel from which a current of steam can be obtained. The steam is passed through the jacket until the temperature of the mercury has reached that of the steam. A mixture of hydrogen and oxygen in the proportions in which they combine, viz., 2 of hydrogen to 1 of oxygen, is then introduced into the eudiometer so that it is filled to the third mark. This must be somewhat above the level of the mercury in the bath, so that the gases in the eudiometer shall be under diminished pressure. On now passing the spark

the gases unite and the water which is formed remains in the form of vapor, as the temperature inside the eudiometer is nearly that of boiling water, and the vapor is under diminished pressure. It is found that the volume of the water vapor is less than that of the gases introduced into the eudiometer. In order to secure the same pressure as that under which the gases were measured, the eudiometer must be lowered until the height of the mercury column in it is the same as it was before the explosion. On now measuring the volume of water vapor, it will be found to be two-thirds that occupied by the uncombined gases. Therefore, 2 volumes of hydrogen combine with 1 volume of oxygen and form 2 volumes of water vapor. It is an
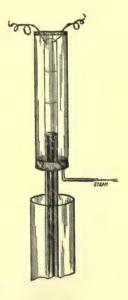


Fɪɢ. 2.

interesting fact that these simple relations exist between the volumes of the combining gases and the volume of the product. We shall see that similar relations hold good in the case of other gases ; and the following general statement is based upon a great deal of careful study :

*When two or more gaseous substances combine to form a gaseous compound, the volumes of the individual constituents as well as their sum bear a simple relation to the volume of the compound.*

This is known as the law of combination by volume. As will be seen farther on, it has a most important bearing upon some of the fundamental ideas held in regard to the constitution of matter.

**Heat Evolved in the Union of Hydrogen and Oxygen.**—To get as complete a knowledge as possible of the reaction which takes place between hydrogen and oxygen we have still to determine the amount of heat evolved. The heat evolved in burning a gram of hydrogen can be determined, and from this we can calculate the heat of formation of water which, according to what was said on page 37, is the amount of heat evolved by the combination of 2 grams of hydrogen with 15.88 grams of oxygen. We are to determine the value of $x$ in the equation

$$[\text{H}_2, \text{O}] = x \text{ cal.,}$$

which expresses in thermochemical language the fact that when 2 grams of hydrogen combine with 15.88 grams of oxygen $x$ calories of heat are evolved.

The determination is made by burning a known weight of hydrogen in a vessel surrounded by water and arranged in such a way that all the heat is absorbed by the water. Experiment has shown that when 1 gram of hydrogen is burned 34,180 calories are evolved. Or,

$$[\text{H}_2, \text{O}] = 68,360 \text{ cal.}$$

No other substance gives as much heat as this in proportion to the weight used.

**Applications of the Heat formed by the Combination of Hydrogen and Oxygen.**—To burn hydrogen in the air is, as we have seen, a simple matter, but to burn it in oxygen requires a special apparatus to prevent the mixing of the gases before they reach the end of the tube where the combustion takes place. The *oxyhydrogen blow-pipe* answers this purpose. This may be constructed in sev-

eral ways, but the simplest is that represented in Fig. 3. It consists of a tube through which a smaller tube passes. The hydrogen is admitted through *a* and the oxygen through *b*. It will be seen that they come together only at the end of the tube. The hydrogen is first passed through and lighted; then the oxygen is passed through slowly, the pressure being increased until the flame appears thin and straight. It gives very little light but is intensely hot. Iron wire, steel, copper, zinc, and other



FIG. 3.

metals burn in the flame with ease. Platinum vessels are made by melting the platinum by means of the oxyhydrogen flame.

**Oxyhydrogen Light.**—When the oxyhydrogen flame is allowed to play upon some substance which it cannot melt or burn, the substance becomes heated so high that it gives off an intense light. The substance commonly used for this purpose is quicklime. Hence the light is often called the lime-light. It is also known as the Drummond light.

The hydrogen is first allowed to pass through the stop-cock, and lighted, when the oxygen is admitted. The flame plays against the piece of lime, and from this the light is given off when it has acquired a high temperature. Coal-gas may be used instead of hydrogen, and it is generally used. Cylinders of compressed coal-gas and of oxygen can be bought, and the gases so prepared are used for the purpose of projecting pictures upon screens in illustrating lectures and for other similar purposes.

**Velocity of Combination of a Mixture of Hydrogen and Oxygen.**—When a mixture of hydrogen and oxygen explodes, the action appears to take place instantaneously throughout the mass. Whether this is really so or not can be determined only by experiment. The action cer-

tainly takes place with great rapidity, and a special apparatus is necessary in order to study the rate of transmission. This subject has been studied by exploding the mixture in long tubes arranged with little movable pistons at various distances. When the explosion reached these points the fact was indicated by motion of the pistons. The result showed that the action is not instantaneous though extremely rapid. The rate of transmission is about 2500 metres per second.

**Summary.**—In our study of the action of hydrogen on oxygen, we have learned : (1) the relations between the weights of the two gases which act upon each other ; (2) the relations between the volumes of the combining gases ; (3) the relations between the volumes of the combining gases and that of the water vapor formed ; (4) the amount of heat evolved when a given weight of hydrogen combines with oxygen ; and (5) that the act of combination of the two gases does not take place instantaneously though with great rapidity. It remains for us to study more carefully the product formed. This is water.

# CHAPTER V.

**Historical.**—Water was long considered an elementary substance until, towards the end of the last century, the discovery of hydrogen and oxygen, and of the nature of combustion, led to the discovery of its composition.

**Occurrence.**—Besides the form in which water occurs in such enormous quantities in the earth, it also occurs in forms and conditions which prevent its immediate recognition. Thus all living things contain a large proportion of water, which can be driven off by heat. If a piece of wood or of meat is heated, liquids pass off, and by purification these can be shown to consist mainly of water. The proportion of water in animal and vegetable substances is very great. If the body of a man weighing 150 pounds were to be put in an oven and thoroughly dried, there would be only about 40 pounds of solid matter left, most of the rest being water.

Water also occurs in another form in which it does not easily reveal its presence. This is as *water of crystallization*. Many chemical compounds found in nature and manufactured are found to give off water when heated. If, for example, the zinc sulphate formed in the preparation of hydrogen from zinc and sulphuric acid is dried by exposure to the air or by pressing between layers of filter-paper, it will be found that, when heated in a dry tube, it gives off water, and at the same time changes its appearance. The same is true of gypsum which is found in nature, and of copper sulphate or blue vitriol. In this last case the loss of water is accompanied by a loss of color. After all the water is driven off, the powder left behind is white.

Many compounds when deposited from solutions in water in the form of crystals combine with definite quan-

tities of water. This water is not present as such, but is held in chemical combination. Hence the substance does not appear moist, though it may contain more than half its weight of water. This water of crystallization is, in some way which is not understood, essential to the form of the crystals. If it is driven off, the crystals generally crumble to pieces. Some compounds combine with different quantities of water under different circumstances, the form of the crystals varying with the quantity of water held in combination.

Compounds differ greatly as regards the ease with which they give up water of crystallization. In general, it is given off when the compound containing it is heated up to the temperature of boiling water. But some compounds give it up by simple contact with the air. This is true of sodium sulphate or Glauber's salt, which contains a quantity of water of crystallization represented by the formula $Na_2SO_4.10H_2O$. If some of the crystals are allowed to lie exposed to the air they undergo a marked change in the course of an hour or two. They lose their lustre and gradually crumble to pieces. Substances which lose their water of crystallization by simple contact with the air are said to be *efflorescent*.

Some compounds if deprived of their water of crystallization will take it up again when allowed to lie in an atmosphere containing moisture. As the air always contains moisture, it is only necessary to expose such compounds to the air in order to notice the phenomenon. It is well shown by the compound calcium chloride, $CaCl_2$. This substance has a remarkable power of attracting water and holding it in combination. If a few pieces are exposed to the air it will be noticed that they soon have a moist appearance, and if they are allowed to lie long enough they will dissolve in the water which is absorbed from the air. Substances which absorb water from the air are said to be *deliquescent*.

**Formation of Water and Proofs of its Composition.**—If we had not already learned, in studying the action of hydrogen upon oxygen, that water is composed of these two gases, we should first subject it to analysis. For

this purpose we should have to bring it under the influence of a number of reagents and study its conduct. If we should pass an electric current through it in the proper way, we should observe that a gas rises from each pole. By placing each pole under the mouth of an inverted tube filled with water the gases are easily collected. When one of the tubes has become full of gas the other one will be only half full. An examination will show that the gas in the tube which is filled is hydrogen, whereas that in the one which is half filled is oxygen. By decomposition of water by means of the electric current, then, there are obtained two volumes of hydrogen for each volume of oxygen. We already know the relative weights of equal volumes of the two gases, so that we can easily calculate the relative weights of the gases obtained in the experiment. The ratio of the weights of equal volumes of hydrogen and oxygen is 1 : 15.88. Therefore, if we have 2 volumes of hydrogen combined with 1 volume of oxygen, the ratio between the weights is 2 : 15.88 or 1 : 7.94. Although we know from the experiment referred to that hydrogen and oxygen are obtained from water in certain proportions, it does not follow that this is the composition of water. For it may be that other elements besides hydrogen and oxygen are contained in it, and it may be also that all the hydrogen and oxygen are not set free by the action of the electric current. We might determine whether either of these possibilities is true or not by decomposing a weighed quantity of water, and weighing the hydrogen and oxygen obtained from it. If we should find that the sum of the weights of hydrogen and oxygen is equal to the weight of the water decomposed, this fact would be evidence that only hydrogen and oxygen are contained in water, and that they are present in the proportions stated. The same thing can be satisfactorily proved by causing hydrogen and oxygen to combine, or by effecting the *synthesis* of water. How this may be done has already been pointed out. It was shown, in the first place, that by burning hydrogen in oxygen water is formed. This proves that water consists of hydrogen and oxygen, but

it does not furnish any proof as to the relation between the quantities of the gases which combine. It is a *qualitative synthesis*. Other methods were described, the object of which was to show in what proportion by weight and by volume hydrogen and oxygen combine to form water. These methods are examples of *quantitative syntheses*. The results proved that to form water hydrogen and oxygen combine in the proportion of 1 volume of oxygen to 2 of hydrogen; and it therefore follows that the decomposition of water which is effected by the electric current is complete.

**Properties of Water.**—Pure water is tasteless and inodorous, and in small quantities colorless. Thick layers are, however, blue. This is seen by filling a long tube with carefully purified water, and examining it by transmitted light, when it appears blue. Some mountain lakes also have a marked blue color. When cooled, water contracts until it reaches the temperature of 4°. At this point it has its maximum density. If cooled below this it expands, and the specific gravity of ice is somewhat less than that of water. Hence ice floats on water. If this were not so there would be great danger in cold climates that the water in the streams would freeze solid. As it is, the lower layers of water are protected by the ice and the cold water just below it, which are poor conductors of heat. Water can be cooled down below its freezing temperature, or 0°, if it is kept perfectly quiet, protected from the air, or cooled in capillary tubes. Water thus cooled down will suddenly solidify when disturbed, and then its temperature rises to 0°. Water boils at 100° under 760 mm. pressure. Increased pressure raises the boiling point, and decreased pressure lowers it.

**Chemical Properties of Water.**—Water is a very stable chemical compound. An indication of the attraction exerted by the hydrogen for the oxygen is given in the great evolution of heat when the two combine. In order to decompose it by heat, as much heat must be added as is evolved when it is formed. At high temperatures it is decomposed into its elements. The decomposition

begins at 1000° and is half complete at 2500°. This kind of gradual decomposition of a compound by heat is called *dissociation.* It is a common phenomenon in chemistry, and farther on we shall have occasion to study it more fully. As has been seen, water is decomposed completely by an electric current, and partly by contact with sodium and potassium at ordinary temperatures, and by iron and carbon at higher temperatures. It combines directly with a large number of substances in the form of water of crystallization, and with others to form definite chemical compounds called hydrates or hydroxides. Thus the oxides of potassium, $K_2O$, and of sodium, $Na_2O$, combine with water with evolution of much heat to form the compounds potassium hydroxide, KOH, and sodium hydroxide, NaOH, which, it will be remembered, are also formed by the action of the elements potassium and sodium on water with liberation of hydrogen. The reactions between the oxides and water are represented by the equations

$$K_2O + H_2O = 2KOH;$$
$$Na_2O + H_2O = 2NaOH.$$

Similarly, lime or calcium oxide, CaO, acts upon water with evolution of heat, as is observed in the process of slaking. The change is like that which takes place with potassium and sodium oxides; and is represented thus:

$$CaO + H_2O = CaO_2H_2 \text{ [or } Ca(OH)_2\text{]}.$$

The product represented by the symbol $Ca(OH)_2$ is known as calcium hydroxide or slaked lime. In the same way barium oxide, BaO, forms barium hydroxide:

$$BaO + H_2O = BaO_2H_2 \text{ [or } Ba(OH)_2\text{]}.$$

We shall meet with many examples of this kind of action in our study of chemical reactions, and we shall see that the hydroxides form two of the most important classes of compounds, known as *acids* and *bases*. The hydroxides of potassium, sodium, calcium, and barium are, for example, bases; while certain hydroxides con-

taining sulphur, nitrogen, and carbon are acids,—such as sulphuric acid $SO_2(OH)_2$, nitric acid $NO_2(OH)$, and carbonic acid, $CO(OH)_2$. It is not believed that water as such is contained in these hydroxides. Nevertheless, when heated many of them give off water. Thus, when heated to a red heat, calcium hydroxide is decomposed into the oxide and water according to the equation

$$Ca(OH)_2 = CaO + H_2O.$$

Many substances which contain hydrogen and oxygen act in the same way. This is due to the great stability of water even at elevated temperatures. As the temperature becomes higher and higher the attraction between the constituents of the compound becomes weaker and weaker. When a point is reached at which the attraction of the hydrogen for the oxygen is greater than that required to hold the constituents together, a rearrangement takes place, and compounds which are stable at the higher temperature are formed.

**Water as a Solvent.**—With a great many substances water forms unstable compounds, the nature of which cannot at present be explained. These unstable compounds are called *solutions*. It is known that many solids, liquids, and gases when brought into water disappear and form colorless liquids which look like water. Some give colored liquids of the same color as the substance dissolved, and others give liquids which have a color quite different from the substance dissolved. On the other hand, there are many substances which do not form such compounds with water or which, as we say, are insoluble in water. In a solution the particles of the substance dissolved are in some way attracted and held in combination by the particles of the liquid. If a very small quantity of substance be dissolved in a large quantity of water and the solution thoroughly stirred, the dissolved substance is uniformly distributed throughout the liquid, as can be shown by refined chemical methods. That the dissolved substance is everywhere present in the solution can be shown further by the aid of certain dye-stuffs, as, for example, fuchsine. A drop of a concen-

trated solution of the substance brought into many gallons of water imparts a distinct color to all parts of the liquid. An experiment of this kind gives some idea of the extent to which the division of matter can be carried. For it is evident that in each drop of the dilute solution there must be contained some of the coloring matter, though the quantity must be what we should ordinarily speak of as infinitesimal. While there seems to be no limit to the extent tò which a solution can be diluted and still retain the dissolved substance uniformly distributed through its mass, there is a limit to the amount of every substance that can be brought into solution, and this varies with the temperature, and, in the case of gases, with the pressure. Some substances are easily soluble, others are difficultly soluble. When the solutions are boiled the water simply passes off and leaves the dissolved substance behind, if it is a non-volatile solid. If, however, the substance in solution is a liquid, a partial separation will take place, the extent of the separation depending largely upon the difference between the boiling-points of the water and the other liquid. A complete separation of two liquids by boiling is difficult and in most cases impossible. If, finally, the substance in solution is a gas, it generally passes off when the solution is heated, though in some cases water is given off leaving the gas in solution, which of course then becomes more concentrated. When a certain concentration is reached a solution of the gas passes over. It is probable that in these cases the gas is in a condition of chemical combination with the water. Solutions, in general, seem to differ from true chemical compounds in some important particulars, and also from mere mechanical mixtures. Definiteness of composition appears to be characteristic of chemical compounds, or, at least, it is characteristic of a large number of compounds which we call chemical compounds. But solutions have no definite composition. We can dissolve any quantity of a substance from the minutest particle to a certain fixed quantity, and the solutions formed are uniform and appear to be just as truly solutions as that which contains the largest quantity which can be

held in combination. On the other hand, in a mere mechanical mixture the constituents may be present in all proportions, while this is not true of solutions. The subject of solution is under investigation, and it has been made highly probable that some substances, when dissolved, are partly or wholly broken down into smaller parts charged with positive and negative electricity respectively. These smaller parts are called *ions*.

**Solution as an Aid to Chemical Action.**—When it is desired to secure the chemical action of one solid substance upon another, it is generally necessary to bring them together in solution. One reason why they do not act readily when mixed in the solid condition is to be found in the fact that, under these circumstances, their particles remain separated by sensible distances, no matter how finely the mixture may be powdered. If, however, the substances are dissolved, and the solutions poured together, the particles of the liquid move so freely among one another that they come in intimate contact, thus facilitating chemical action. Many substances which do not act upon one another at all when brought together in dry condition act readily when brought together in solution. It is believed that this is due principally to the splitting of the compounds into *ions* by the action of the water. These ions being free are capable of acting upon other ions which may be brought into the same solution. This idea will be developed farther on in other connections. Although it is highly probable, then, that when a reaction takes place in a water solution the water itself plays a very important part, the reaction is generally represented by an equation in which the water does not appear. Of course, such an equation is imperfect, but it answers certain purposes quite satisfactorily, and may be used without danger of confusion. Thus, when hydrochloric acid acts upon zinc, hydrogen is liberated and zinc chloride is formed. What we call hydrochloric acid in the laboratory is the liquid which is formed by the absorption of hydrochloric acid gas, HCl, by water. When this liquid is used, however, the chemical act which makes itself

known to us is that which gives hydrogen gas and zinc chloride in solution. Apparently this reaction is independent of the water, and it may be represented thus :

$$Zn + 2HCl = ZnCl_2 + 2H.$$

Sometimes such reactions are written as follows in order to express the fact that water is present, though, as will be observed, no attempt is made to tell what part the water plays :

$$Zn + 2HCl + Aq = ZnCl_2 + 2H + Aq ; \text{ or}$$
$$Zn + 2HCl + H_2O = ZnCl_2 + 2H + H_2O.$$

There is no objection to this, certainly, but it is questionable whether, considering the purposes for which chemical equations are used, this increases their value.

**Natural Waters.**—All water found in nature is more or less impure or, in other words, contains something in solution. In the first place, waters which are exposed to the air dissolve some of the gases of which the air is composed, as oxygen, nitrogen, and carbon dioxide. Again, natural waters necessarily are in contact with the earth, they always dissolve some of the earthy substances ; and, finally, many waters come in contact with animal and vegetable substances and dissolve something from these. The water which is carried up as vapor from the surfaces of natural bodies of water is approximately pure. When this is precipitated as rain it dissolves certain substances from the air, and the first rain that falls during a storm is always more or less contaminated. In a short time, however, the air becomes washed and the rain which falls thereafter is approximately pure water. If it remains in contact with insoluble rocks, as, for example, quartzite or sandstone, it remains pure, and mountain-streams which flow over sandstone beds are, in general, the purest. Water which flows over limestone dissolves some of this and becomes " hard." A similar change is brought about in water by contact with gypsum and magnesium sulphate. The condition of hardness will be taken up more fully under calcium and magnesium compounds. The many varieties of mineral

springs have their origin in the presence in the earth of certain substances which are soluble in water. Among those most frequently met with in solution in natural waters are carbonic acid, sodium carbonate, sodium sulphate or Glauber's salt, sodium chloride or common salt, magnesium sulphate, iron carbonate, and sulphuretted hydrogen. *Effervescent* waters are those which contain a large quantity of carbonic acid in solution and give off carbon dioxide gas when exposed to the air. *Chalybeate* waters are those which contain some compound of iron in solution; *sulphur* waters contain the gas, sulphuretted hydrogen. Common salt occurs in large quantities in different parts of the earth. As it is easily soluble in water, many streams contain it; and as most streams find their way to the ocean, we see one reason why the water of the ocean should be salt.

As streams approach the habitation of man they are subjected to a serious cause of contamination. The drainage from the neighborhood of human dwellings is very apt to find its way into a near stream. The substances thus carried into the stream undergo decomposition and give rise to the formation of larger or smaller quantities of new products some of which have the power to produce disturbances when taken into the system, and others to produce disease. This condition of things is most strikingly illustrated by the case of a large town situated on the banks of a river. It frequently happens that the water of the river is used for drinking purposes, and it also frequently happens that the water is contaminated by drainage. River water when once contaminated by drainage tends to become pure again by contact with the air, the change consisting largely in the slow oxidation of the substances which are of animal or vegetable origin, and their conversion into harmless products. If water is to be used for drinking purposes, however, it is not well to rely too much upon this process of purification. So much has of late years been said about drinking-water that excessive alarm has been created, and water is no doubt frequently held responsible for sickness with which it has nothing to do. In some places the war against the water supply has been carried so far that those who

can afford it drink only artificially purified and distilled water. It is undoubtedly well to be cautious, but it is possible to be too cautious.

**What Constitutes a Bad Drinking Water.**—A good drinking water should be free from odor and taste and should not contain anything which can act injuriously upon the system. It is, however, difficult to decide by chemical means whether the water contains anything injurious or not, as there may be a very minute quantity of an extremely injurious substance, for example a disease germ, present, and chemical analysis would be powerless to detect it. On the other hand, water which is very considerably contaminated by sewage may be harmless, and yet the latter might be pronounced " bad " and the former " good." The rule generally adopted by chemists in dealing with water is to pronounce any water dangerous which is contaminated by sewage. Such contamination can generally be detected by analysis or by analysis and inspection of the sources.

**Purification of Water.**—Impure water may become purer by natural methods as has been stated, and it may be rendered fit for drinking purposes by filtering through such substances as charcoal, sand, spongy iron, etc. A filter, no matter of what it may be made, will not, however, remain efficient for any length of time, as the substances contained in the impure water are retained by it and, after a time, it becomes a source of pollution instead of a purifier. For refined work in chemistry pure water is prepared by distilling natural waters. The process of distillation consists in boiling the water and then passing the steam through a tube or system of tubes surrounded by cold water. Thus the steam is condensed, and the distilled water is approximately pure. Of course, it is necessary that the tubes in which the condensation takes place should be of such material that water does not act upon it to any extent. The materials used are glass, block tin, and platinum. Chemically pure water is a very rare substance even in the best chemical laboratories. The slight impurities present in ordinary distilled water are not, however, of special importance under ordinary circumstances.

# CHAPTER VI.

## CONSTITUTION OF MATTER—ATOMIC THEORY—ATOMS AND MOLECULES—CONSTITUTION—VALENCE.

**Early Views.**—In early times two views were held regarding the ultimate constitution of matter. The first was, that matter is infinitely divisible—that there is no limit to the process of subdivision; the other was, that there is a limit to the divisibility—that when certain inconceivably small particles are reached the process must stop. These small particles were called *atoms,* meaning indivisible. As long as the constitution of matter was merely a subject of speculation, the atoms remained without a physical basis and were only metaphysical conceptions. The facts which come under our ordinary observation do not furnish any evidence for or against the existence of atoms; and, though we discuss the subject indefinitely, little or no progress can be made without refined observations on the properties of matter. So it was, that until the beginning of the present century the atomic theory remained practically what it was when first proposed, and as such it was of **no value to chemistry.**

**The Atomic Theory as proposed by Dalton.**—We have seen how Dalton, at the beginning of this century, discovered the law of multiple proportions. This law, as well as that of definite proportions, required explanation. The questions to be answered are: (1) Why do the elements combine in definite proportions? (2) Why, when elements combine with each other in more than one way, do the relative quantities which enter into combination in the different cases bear simple relations to one another? and (3) What is the significance of the figures representing the combining weights? Dalton saw that the facts referred to could be explained by the atomic theory, while, on the theory that matter is infinitely divisible, they

appear to be inexplicable. It is only necessary to assume that each element is made up of particles which are not divisible in chemical processes, and that these particles, or atoms, have definite weights. The atoms of any one element must be supposed to have the same weight, while the atoms of different elements have different weights. Now, when chemical combination takes place, Dalton supposed that the action was between the atoms. The simplest case is that in which combination takes place in such way that each atom of one element combines with one atom of another ; but, besides this kind of combination, we may have that in which one atom of one element combines with two atoms of another, or two of one may combine with three of another, etc. Suppose two elements $A$ and $B$, the weights of whose atoms are to each other as $1 : 10$, are brought together, and they combine in the simplest way, i.e., one atom of one with one atom of the other, then it is plain that in the compound $AB$ the elements will be contained in the proportion of 1 part of $A$ to 10 parts of $B$, whether a small or a large quantity of the compound is formed, and no matter in what proportions the elements are brought together. If they should be brought together in the proportion of their atomic weights ($1 : 10$), then no part of either element will be left uncombined after the act of combination has taken place. If, however, a larger proportion of either element is taken than that stated, then the quantity of the one which is in excess of this proportion will be left uncombined. This is in accordance with what we know takes place, and it is a conclusion drawn from the theory. No matter how many atoms of $A$ we may take, the same number of atoms of $B$ will be required to combine with all of them. But each atom of $B$ weighs 10 times as much as each atom of $A$, therefore the total mass of $B$ which enters into combination must be 10 times that of $A$ with which it combines. It may be, however, that these same elements can form other compounds with each other. If $A$ and $B$ represent the atoms of the elements and we assume these atoms to be chemically indivisible, then the other compounds must be represented by such

symbols as $AB_2$, $A_2B$, $AB_3$, $A_3B$, $A_2B_3$, etc., which repre-
sent compounds in which 1 atom of $A$ is combined with
2 atoms of $B$; 2 of $A$ with 1 of $B$; 1 of $A$ with 3 of $B$;
3 of $A$ with 1 of $B$; 2 of $A$ with 3 of $B$; etc.: or they
also represent compounds in which 1 part by weight of
$A$ is combined with 20 parts by weight of $B$; 2 parts of
$A$ with 10 of $B$; 1 of $A$ with 30 of $B$; 3 of $A$ with 10 of
$B$; 2 of $A$ with 30 of $B$; etc. It is therefore clear that,
if the atomic theory as put forward by Dalton is true, the
elements must combine according to the laws of definite
and multiple proportions; and it appears that the figures
which represent the combining weights of the elements
must either bear to one another the same relation as the
weights of the atoms, or, at all events, the atomic weights
or the relative weights of the atoms must be closely re-
lated to the combining weights, as will be pointed out
more clearly presently.

**Use and Value of a Theory.**—The relation of a theory
to facts is very simple, but is frequently misunderstood.
The relation may be conveniently illustrated by the case
under consideration. By a careful investigation of a
number of chemical compounds it was shown that in each
of them the same elements always occurred in the same
proportion. This led to the belief that this is true of
every chemical compound, and after further investigation
which, as far as it went, showed the surmise to be correct,
the law of definite proportions was proposed. This law
is simply a statement of what has been found true in all
cases examined. It involves no speculation. It is a
statement of fact. It may be said that the statement or
law must be open to some doubt for the reason that all
possible cases have not been examined, and it may not
hold true for some of these unexamined cases. The reply
to this is that it has been found true in a very large num-
ber of cases and in all cases which have been investigated.
It is true for the present state of our knowledge, and that
is all we can demand of any law. Again, further investi-
gation led to the discovery of the law of multiple propor-
tions, which is also a statement of what has been found
true in all cases investigated. It, like the law of definite

proportions and in the same sense, is a statement of fact. But having gone thus far, we now ask, what is the explanation of these laws? We simply know the facts—what is the explanation? By experiment we cannot go beyond these facts, but it is possible to imagine a cause and then proceed to see whether the imagined cause is sufficient to account for the facts. This is what Dalton did. He imagined that matter is made up of atoms of definite weights, and that chemical combination takes place in simple ways between these atoms. This imagined cause is the *atomic theory*. It is not a statement of anything found by investigation. It is not a statement of an established fact. It may or may not be literally true, but at all events it is the best guess that has ever been made as to the cause of the fundamental laws of chemical action, and it furnishes a very convenient means of interpreting the facts of chemistry. Since the atomic theory was first proposed it has been accepted by nearly all chemists. It has been of great value in suggesting methods of work, and has contributed largely to the advance of chemistry. Any theory which is in accordance with the facts and leads to the discovery of new facts is of value, whether it should eventually prove to be true or false. At the same time a false theory may do much harm, as it may lead men to misinterpret the facts which they observe, and thus retard progress.

**Atomic Weights and Combining Weights.**—If the atomic theory is true the atoms of each element must have definite weights, and the determination of these atomic weights must evidently be of great importance. By analysis of compounds we can only determine the proportions by weight in which the elements combine with one another. Can we in this way determine the atomic weights? In the first place, it is clear that it is out of the question to think of determining the absolute weights of the atoms, and all that we can possibly do is to determine their relative weights. As of all the elements hydrogen enters into combination in smallest relative quantity, its atomic weight is taken as the unit of the system, and the problem before us is to determine how many

times heavier the atoms of the other elements are than
that of hydrogen. If every element combined with hydro-
gen in only one proportion the problem would be a com-
paratively simple one. Thus the three elements chlorine,
bromine, and iodine combine with hydrogen, forming only
one compound each. On analysis these are found to
contain respectively

1 part of hydrogen to   35.18 parts of chlorine ;
1   "           "      "    79.34    "    " bromine ; and
1   "           "      "  125.89    "    " iodine.

There is no reason for believing that in these compounds
the elements are combined in any but the simplest way,
i.e., that each atom of hydrogen is combined with one
atom of chlorine to form hydrochloric acid, etc. If this
is true, then the atom of chlorine must weigh 35.37 times ;
that of bromine 79.76 times ; and that of iodine 126.54
times as much as that of hydrogen, or, in other words,
the atomic weights of chlorine, bromine, and iodine are
respectively 35.37, 79.76, and 126.54. It will, however,
be observed that there is no evidence as to whether the
elements in these compounds are combined in the simplest
way or not. It is possible, as far as we know, that one
atom of hydrogen may combine with two or three of
chlorine, or that one of chlorine may combine with two
or three of hydrogen. As there is, however, no evidence
upon this point the simplest assumption is made.

If we take the case of oxygen the problem is more com-
plex. In water the elements are combined in the propor-
tion of 7.94 parts of oxygen to 1 part of hydrogen, and
from this we should naturally conclude that the atomic
weight of oxygen is 7.94 ; but further study shows that
this conclusion is not justified. Hydrogen and oxygen
form a second compound known as hydrogen dioxide or
hydrogen peroxide in which there are 15.88 parts of oxy-
gen to 1 of hydrogen. This may be explained in the
terms of the atomic theory by assuming that water is
represented by the formula $HO$, and hydrogen dioxide
by $HO_2$. But it may be that the atomic weight of oxygen
is 15.88, and then water must be represented by the

formula $H_2O$, and hydrogen dioxide by HO. Simple analysis of the compounds is not sufficient to enable us to decide between these possibilities. It is, therefore, evident that in order to determine the atomic weights something besides the determination of the composition of compounds is necessary. The figures representing the combining weights found in this way will, however, either be identical with the atomic weights or will bear a simple numerical relation to them.

**Molecules.**—Investigation of certain phenomena of light, of electricity, of liquid films and the conduct of gases has led physicists to the conclusion that matter is not continuous, but made up of small particles, which are called *molecules*. A gaseous molecule is defined as "*that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.*" It would be out of place here to present the physical facts upon which the molecular theory rests. Suffice it to say that it is the only theory which has been found adequate to account for the behavior of gases.

**Avogadro's Law.**—The fact that gases conduct themselves in the same way under the influence of changes in temperature and pressure can only be explained by assuming that *equal volumes of all gases and vapors contain the same number of ultimate particles or molecules at the same temperature and pressure.*

This is a deduction from the well-tested molecular theory of gases. It was, however, originally put forward by the Italian chemist Avogadro from a study of chemical as well as of physical facts, and a little later it was suggested as probable by the French physicist Ampère. It is therefore generally spoken of as Avogadro's law, and sometimes as Ampère's law. Absolute proof of its truth cannot be given, but it is in thorough accordance with a large number of well-known facts, and it is undoubtedly true, if the molecular theory of matter is true. It may therefore be considered as furnishing a solid foundation for further conclusions bearing upon the problem of the determination of the atomic weights.
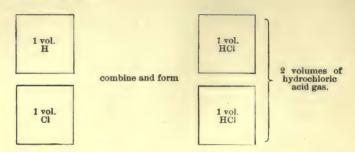
**Distinction between Molecules and Atoms.**—If we consider any chemical compound, as water or hydrochloric acid, it is evident that the smallest particle or the molecule of the compound must be made up of still smaller particles. Thus, the smallest particle of water must contain smaller particles of hydrogen and oxygen, and the smallest particle of hydrochloric acid must contain smaller particles of hydrogen and chlorine. These smallest particles of the molecules are the atoms. The molecules of the compounds are, according to this view, made up of the atoms of the elements. Similarly the elements themselves are, for good reasons which will be presented, believed to consist of molecules which are in turn made up of atoms of the same kind, though in a few cases the molecule of the element is identical with the atom. The difference between a compound and an element then is, in general, that the molecule of the compound consists of atoms of different kinds, while the molecule of an element consists of atoms of the same kind or, in a few cases, of one atom. Generally the atoms do not exist in the free or uncombined state, but, if they are set free by chemical action, they unite to form molecules. The following may serve as a definition of the conception of atoms at present held by chemists:

*Atoms are the indivisible constituents of molecules. They are the smallest particles of the elements that take part in chemical reactions, and are, for the greater part, incapable of existence in the free state, being generally found in combination with other atoms, either of the same kind or of different kinds.*

It cannot be too strongly emphasized that the views held in regard to the relations between molecules and atoms are based upon an enormous amount of painstaking study of facts, and in order fully to comprehend their value a study of most of these facts would be necessary. These views have gradually become firmly established as knowledge of the facts has grown more and more profound. Accepting them, we are now to see how they aid us in the problem with which we are dealing, viz., the determination of the atomic weights.

**Molecular Weights.**—If equal volumes of gases contain the same number of molecules at the same temperature and pressure, it is only necessary to determine the weights of equal volumes of gases to learn the relative weights of their molecules. Thus, if we weigh a liter of each of three gases, and find that the weights are to one another as 1 to 2 to 3, then it follows that the relation between the weights of the molecules of these gases is expressed by these figures, or, in other words, the molecule of the second gas is twice as heavy; and that of the third gas is three times as heavy as that of the lightest. The determination of the relative weights of the molecules of substances which either are gaseous or can be converted into gases resolves itself simply into a determination of the weights of equal volumes. In representing the molecular weights we may use any figures which are most convenient, provided only that they bear to one another the relations determined by experiment. If, however, we call the atomic weight of hydrogen 1, then our system of molecular weights must be based upon this, and the molecular weight of a compound should state how much heavier the molecule is than an atom of hydrogen. Thus, if we say that the molecular weights of water and hydrochloric acid are respectively 17.88 and 36.18, we mean that, if the hydrogen atom weighs 1, then the weights of the molecules of water and hydrochloric acid are represented by the figures given. Now, if the molecule of hydrogen were identical with the atom or, in other words, if the molecular weight were equal to 1, then the adjustment of the system of molecular weights to the atomic weight of hydrogen would be perfectly simple. It would only be necessary to determine the weight of a given volume of hydrogen and compare the weights of equal volumes of other gases with it. If the weight of a certain volume of any compound should be found to be 10 times that of an equal volume of hydrogen, it would follow that the molecular weight of the compound is 10. But the molecule and atom of hydrogen are not identical, as can be shown without difficulty. When a given volume of hydrogen combines with chlorine it combines with

an equal volume of this element, and the two volumes which combine form an equal volume of the compound hydrochloric acid. These facts may be graphically represented as follows :



Now, bearing in mind Avogadro's law that equal volumes of all gases contain the same number of molecules, it follows that if, in the volume of hydrogen taken, there is any finite number of molecules, say 100, then in the same volume of chlorine there must be 100 molecules, and in the two volumes of hydrochloric acid gas obtained there must be 200 molecules of the compound. Therefore, from 100 molecules of hydrogen and 100 molecules of chlorine there are formed 200 molecules of hydrochloric acid. But in each molecule of hydrochloric acid there must be at least one atom of hydrogen and one atom of chlorine, and in the 200 molecules there must be at least 200 atoms of hydrogen and 200 atoms of chlorine. Now, these 200 atoms of hydrogen have come from the 100 molecules, and the same is true of the chlorine. It, therefore, follows that *each molecule of hydrogen and each molecule of chlorine must consist of at least two atoms.* Or, we may say that, if there is one atom of hydrogen in the molecule of hydrochloric acid, then there are two atoms of hydrogen in the molecule of hydrogen. The assumption that the molecule of hydrogen is twice as heavy as the atom is found to satisfy every requirement of the present state of our knowledge. From the above, the following rule for the determination of molecular weights is deduced : Determine the specific gravity of the substance in terms of hydrogen and multiply the

result by 2. Thus the specific gravity of water vapor in terms of hydrogen is 8.94, or, in other words, a given volume of water vapor weighs 8.94 times as much as the same volume of hydrogen. But the molecular weight of hydrogen being 2, that of water must be 17.88. As the specific gravity of gases is frequently stated in terms of the air standard, it is desirable to know the relation between these figures and those based upon hydrogen. The specific gravity of hydrogen as compared with air is 0.06926; when taken as the standard it is represented by 1. But $1 \div 0.06926$ is 14.44; therefore, to convert the specific gravities on the air standard into those on the hydrogen standard it is only necessary to multiply by 14.44. Thus the specific gravity of water vapor, air being the standard, is 0.623. To find its specific gravity, hydrogen being the standard, multiply by 14.44. Now 0.623 $\times$ 14.44 is very nearly 9. This being the specific gravity, the molecular weight is obtained by multiplying by 2. Of course, we should reach the same result by multiplying the specific gravities in terms of air directly by 28.88. Below are given the molecular weights of a few elements and compounds which have been determined by the method just described:

| Name. | Sp. Grav. H = 1. | Molec. Weight. | Molecular Formula. |
|---|---|---|---|
| Hydrogen | 1 | 2 | $H_2$ |
| Nitrogen | 13.93 | 27.86 | $N_2$ |
| Water | 8.94 | 17.88 | $H_2O$ |
| Hydrochloric acid | 18.09 | 36.18 | $HCl$ |
| Ammonia | 8.46 | 16.93 | $NH_3$ |
| Marsh gas | 7.96 | 15.92 | $CH_4$ |
| Carbon monoxide | 13.90 | 27.80 | $CO$ |
| Carbon dioxide | 21.84 | 43.68 | $CO_2$ |

**Deduction of Atomic Weights from Molecular Weights.—** The determination of molecular weights does not necessarily carry with it the determination of the atomic weights. It is plain from what has already been said that a knowledge of the molecular weight of an element does not convey a knowledge of its atomic weight. If,

for example, we learn that the molecular weight of nitrogen is approximately 28, we have no means of judging from this what the atomic weight is. It is plainly necessary to know of how many atoms each molecule of nitrogen is made up, and to learn this is not a simple matter. It is easier to determine the atomic weight of an element through a study of its compounds. Suppose it is desired to determine the atomic weight of oxygen. We first determine the molecular weights of a number of compounds which contain oxygen, and then analyze these compounds. We then see what the smallest figure is that is required to express the weight of the oxygen that enters into the composition of the molecules, and this figure is selected as the atomic weight. The molecular weights and the composition of several oxygen compounds are given in the following table:

| Compound. | Mol. Wt. Approx. | Composition. | | |
|---|---|---|---|---|
| Water ........................... | 17.88 | 2 | parts | hydrogen, |
| | | 15.88 | " | oxygen. |
| Carbon monoxide................. | 27.80 | 11.92 | " | carbon, |
| | | 15.88 | " | oxygen. |
| Carbon dioxide.................... | 43.68 | 11.92 | " | carbon, |
| | | 31.76 | " | oxygen. |
| Nitric oxide ...................... | 29.81 | 13.93 | " | nitrogen, |
| | | 15.88 | " | oxygen. |
| Nitrous oxide...... .. ........... | 43.74 | 27.86 | " | nitrogen, |
| | | 15.88 | " | oxygen. |
| Sulphur dioxide................... | 63.59 | 31.83 | " | sulphur, |
| | | 31.76 | " | oxygen. |
| Sulphur trioxide.................. | 79.47 | 31.83 | " | sulphur, |
| | | 47.64 | " | oxygen. |

The figures in the third column are of course determined by analysis, an example of the methods used having been given in the chapter on water. Stated in ordinary language, the figures in the case of carbon monoxide mean that the molecule of this compound weighs 27.80 times as much as the atom of hydrogen, and the 27.80 parts of matter are made up of 11.92 parts of carbon and 15.88 parts of oxygen. Considering now the composition of the compounds in the table, it will be seen that the smallest mass of oxygen which enters into the composition of any of the

molecules weighs 15.88 times as much as the atom of hydrogen. We find twice this mass as in carbon dioxide and sulphur dioxide; and three times as in sulphur trioxide, but no smaller mass. Now, if we should examine all compounds of oxygen which can exist in the form of gas or vapor we should find the same thing true; that is to say, the smallest mass of oxygen which enters into the composition of molecules is 15.88 as great as that of the atom of hydrogen. The conclusion is therefore drawn that 15.88 is the atomic weight of oxygen. The possibility that the atomic weight of oxygen is less than this figure is not excluded. It may be that in the simplest oxygen compounds now known there are two or more atoms of this element in the molecules. But in the total absence of evidence on this point all we can do is to accept the figure 15.88 as in perfect accordance with all our knowledge of oxygen compounds.

In this way the atomic weights of all elements which form gaseous compounds or compounds that can be converted into vapor have been determined; and the determinations made in this way are regarded as the most reliable.

**Exact Atomic Weights determined by the Aid of Analysis.**—By determining molecular weights it is possible to decide approximately what figure represents the atomic weight of an element, but the methods employed in making determinations of molecular weights are liable to slight errors, and therefore the atomic weights obtained directly from the molecular weights deviate slightly from the true figures. In order to determine the atomic weights with the greatest possible accuracy, the most refined methods of chemical analysis are brought into play, and the figures in the table on page 21 have been determined in this way by a combination of a study of the specific gravity of gases and by the most careful analyses, together with some other methods which will be taken up later.

**Molecular Formulas.**—The symbols of chemical compounds first used were intended to express simply the composition of the compounds, and this can be done as was explained in Chapter I. by adopting a system of

combining weights of the elements. According to the
theory explained in the last chapter the smallest particle
of every compound is a molecule, and each molecule is
made up of atoms. It appears, therefore, desirable for
the sake of uniformity that the symbols used to repre-
sent chemical compounds should represent molecules.
Where the molecular weight of a compound, the atomic
weights of the elements of which it is composed, and its
composition are known, there is no difficulty in represent-
ing it by a molecular formula. Thus, the molecular
weight of ammonia is found by experiment to be approxi-
mately 17, and the 17 parts are made up of 14 parts of
nitrogen and 3 parts of hydrogen. The atomic weight
of nitrogen is found by the method which has just been
described to be very nearly 14. Therefore the mole-
cule of ammonia weighing 17 parts is composed of 1
atom of nitrogen weighing 14 parts and 3 atoms of hy-
drogen weighing 3 parts. The composition of the mole-
cule is therefore represented by the formula $NH_3$. Simi-
larly the composition of the molecule of water is repre-
sented by the formula $H_2O$; that of hydrochloric acid
by HCl; that of marsh gas by $CH_4$; etc., etc. Every
formula now in use is intended to represent a molecule of
the compound for which it stands. In regard to the
molecular weights of compounds that are not gaseous
nor convertible into vapor, Avogadro's method is plainly
of no avail. Methods have, however, been devised which
are applicable to a number of these (see Chapter XXIII).

Constitution.—When hydrochloric acid is formed, we
conceive that each atom of hydrogen combines with one
atom of chlorine, and that the molecules of the resulting
compound are made up each of an atom of hydrogen and
an atom of chlorine. What the act of combination con-
sists in we do not know. We simply know that something
very remarkable takes place, and that as a consequence
the hydrogen and chlorine cease to exist in their original
forms. It is idle at present even to speculate in regard
to the character of the change. The fact of union is ex-
pressed by writing the symbols of the elements side by
side without any sign between them, as HCl, or, some-

times, it is convenient to use a line to indicate chemical union, thus: H–Cl. According to the molecular theory the molecule of water consists of two atoms of hydrogen and one of oxygen, as represented by the formula $H_2O$, and the question now suggests itself whether all three atoms are in combination with one another or whether each of the hydrogen atoms is in combination with the oxygen atom, but not with each other, as represented by the formula H–O–H. So too in the case of ammonia, the molecular formula of which is $NH_3$, the question suggests itself: Are the three atoms of hydrogen in combination with the atom of nitrogen, but not with one an-

other, as represented in the formula $N{\Large\langle}\begin{smallmatrix}H\\H\\H\end{smallmatrix}$? It is ex-

tremely difficult to answer such questions, but, at the same time, certain facts are known which enable us to draw probable conclusions. Formulas which express the composition of molecules and at the same time express the relations or the connections which exist between the atoms are called *constitutional formulas*. These constitutional formulas are very frequently used at present, but sometimes without a sufficient basis of facts to justify them. Whenever they are used in this book, the reasons for them will be stated as fully as may appear necessary.

**Valence.**—The formulas of the hydrogen compounds of chlorine, oxygen, nitrogen, and carbon, all determined by the same method, are

$$ClH \qquad OH_2 \qquad NH_3 \qquad CH_4.$$

A consideration of these formulas and of many similar ones has led to the belief that the atoms of different elements differ in their power of holding other atoms in combination. The simplest explanation of the composition of the compounds above represented is that the atoms of chlorine, oxygen, nitrogen, and carbon differ in their power of holding hydrogen atoms in combination. Hydrogen and chlorine combine in only one way, 1 atom of chlorine combining with 1 of hydrogen; 1 of oxygen

combines with 2 of hydrogen; 1 of nitrogen with 3 of hydrogen; and 1 of carbon with 4 of hydrogen. The limit of the combining power of the atom of chlorine is reached when it has combined with one atom of hydrogen. And as one chlorine atom can hold but one atom of hydrogen in combination, so one atom of hydrogen can hold but one atom of chlorine. Either the hydrogen atom or the chlorine atom may be taken as an example of the simplest kind of atom. Any element like hydrogen or chlorine is called a *univalent element ;* an element like oxygen whose atom can hold two unit atoms in combination is called a *bivalent element ;* an element like nitrogen whose atom can hold three unit atoms in combination is called a *trivalent element ;* and an element like carbon whose atom can hold four unit atoms in combination is called a *quadrivalent element.* Most elements belong to one or the other of these four classes, though there are some which can hold five, six, and even seven unit atoms in combination. These are called *quinquivalent, sexivalent,* and *septivalent* respectively.

*Valence* is defined as that property of an element by virtue of which its atom can hold a definite number of other atoms in combination. In the formation of compounds the valence of the elements determines how many atoms of any element can enter into combination with any other. The atoms are sometimes spoken of as having bonds which are graphically represented by lines. Thus, a univalent element is said to have one bond, as represented by H–, Cl–, etc. ; a bivalent element is said to have two bonds, –O–, –S–, etc. ; a trivalent element three, $-\overset{\mid}{\text{N}}-$ ; and a quadrivalent element four, $-\overset{\mid}{\underset{\mid}{\text{C}}}-$. Of course, this is merely a symbolical representation of the idea that each atom has a definite power of combining with others. It is further said that when the atoms unite these bonds become satisfied. Thus when one atom of hydrogen unites with one of chlorine, the bond of each is regarded as uniting with the bond of the other, and this is represented by the symbol H–Cl. So too, when two atoms of hydrogen unite with one of oxygen, the com-

pound is represented in this way : H–O–H or $O<{}^H_H$.    In the union of atoms, further, to use the figurative language, two bonds may be satisfied by two univalent atoms or by one bivalent atom.   Thus, in marsh gas, $CH_4$, the four affinities or bonds of the quadrivalent carbon atom are regarded as being satisfied by the four univalent hydrogen atoms.   In the compound $H–\overset{H}{\underset{|}{C}}=O$, however, two of the bonds are regarded as satisfied by two univalent hydrogen atoms, and the other two by one bivalent oxygen atom ; and, again, in the compound $O=C=O$, the four bonds of the carbon atom are regarded as satisfied by two bivalent oxygen atoms.

**Replacing Power of Elements.**—As has been seen, when potassium acts upon water the action is represented by the equation

$$K + H_2O = KOH + H.$$

Expressing this reaction by means of formulas which take the valence of the elements into consideration we have the following :

$$K + H–O–H = K–O–H + H.$$

According to this, one atom of potassium is substituted for one atom of hydrogen in water, and, in the compound formed, the atom of potassium is regarded as occupying the place of the hydrogen atom.   The elements calcium and barium are bivalent like oxygen, as shown in the compounds $CaCl_2$ and $BaCl_2$, in which the atom of calcium as well as that of barium holds two univalent atoms of chlorine in combination.   When these elements act upon water, hydrogen is liberated as with potassium, but each atom replaces two atoms of hydrogen, as represented in the equations

$$Ca + 2H_2O = CaH_2O_2 + 2H ;$$
$$Ba + 2H_2O = BaH_2O_2 + 2H.$$

Or expressing the changes by valence formulas, we have

$$Ca + \frac{H\text{–}O\text{–}H}{H\text{–}O\text{–}H} = Ca{<}_{O\text{–}H}^{O\text{–}H} + H_2 \, ;$$

$$Ba + \frac{H\text{–}O\text{–}H}{H\text{–}O\text{–}H} = Ba{<}_{O\text{–}H}^{O\text{–}H} + H_2 .$$

A trivalent element acting in the same way would give a compound of the general formula $M{\displaystyle{<\atop<}}\begin{smallmatrix}O\text{–}H\\O\text{–}H\\O\text{–}H\end{smallmatrix}$, in which M represents any trivalent element.

So, too, in the action of various elements upon hydrochloric acid, HCl, a univalent element like sodium or potassium replaces one hydrogen atom in one molecule of the acid, and forms a compound of the general formula MCl, as, for example, KCl and NaCl. A bivalent element, like zinc, replaces two atoms of hydrogen in two molecules of the acid, forming the compound $ZnCl_2$:

$$Zn + \frac{HCl}{HCl} = Zn{<}_{Cl}^{Cl} + H_2 .$$

A trivalent element forms a compound of the general formula $MCl_3$, as, for example, aluminium chloride :

$$Al{<}\begin{smallmatrix}Cl\\Cl\\Cl\end{smallmatrix} .$$

The above explanation of the hypothesis of valence will suffice by way of introduction to the subject. The relation which it bears to the facts is simply this : On studying the composition of chemical compounds we find that, in general, the elements combine with one another in comparatively few proportions. Thus, hydrogen and chlorine combine with each other in only one proportion ; hydrogen and oxygen in two ; nitrogen and hydrogen in four ; etc. There is something limiting the complexity of compounds. We might study the laws governing the complexity of compounds without any hypothesis as to the cause, but the hypothesis of valence is a convenient explanation of these laws, and it has been of much service in furnishing chemists with a simple language for representing chemical changes.

# CHAPTER VII.
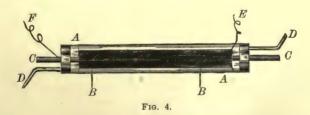
OZONE — ALLOTROPY — NASCENT STATE — HYDROGEN
DIOXIDE.

**Occurrence.**—Ozone has long been thought to be pres-
ent in the air in small quantity, but careful research has
made this occurrence appear doubtful.

**Preparation.**—It was observed in the last century that,
when a powerful electric machine is worked in a room,
something is formed which has a strong odor, and the
same odor was noticed during thunder-showers. After-
wards the same thing was noticed when water is decom-
posed by an electric current, and when phosphorus is ex-
posed to moist air. The substance was at first supposed
to be a compound of water and oxygen, but long-contin-
ued investigation showed that it could be made from pure
dry oxygen, and that by heat and other means it is de-
composed into nothing but ordinary oxygen.

It is prepared mixed with oxygen by passing electric
sparks through ordinary oxygen in an apparatus con-
structed on the principle of that represented in Fig. 4.



FIG. 4.

*A A* is a glass tube about an inch in diameter closed at
the ends with brass caps or with corks, covered with shel-
lac on the inner side. A metallic cylinder *BB* covered
with tin-foil is placed inside this tube. The cylinder is
connected with the tubes *CC*, and through these and the

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cylinder a current of cold water is kept flowing. The oxygen passes through the glass tube by means of the tubes *DD*, and necessarily passes through the narrow space between the glass tube and the metallic cylinder. Around the outside of the glass tube is wound a strip of tin-foil. By means of the wires *F* and *E* connection is established with the poles of an induction-coil, or a Holtz electrical machine.

Ozone is also made by placing a few pieces of phosphorus in the bottom of a good-sized bottle and partly covering them with water; and, finally, it is made by treating barium dioxide, $BaO_2$, and some other compounds rich in oxygen with sulphuric acid.

**Properties.**—Ozone is a gas which can be condensed to the liquid form, the liquid having a blue color. It has a strong odor, and acts in an irritating way upon the membranes lining the throat. Its chemical conduct is entirely different from that of oxygen. While the latter at ordinary temperatures is not an active element, ozone is. It acts upon most substances of animal or vegetable origin, and oxidizes nearly all the metals, besides producing a variety of other changes which are not produced by oxygen at the ordinary temperature. Among the characteristic changes which may be made use of for the purpose of detecting ozone are the following: (1) It liberates iodine when brought in contact with potassium iodide; the action being represented thus:

$$2KI + H_2O + O = 2KOH + 2I.$$

Now, iodine has the power to turn starch blue. Therefore, if ozone is brought into a solution containing starch and potassium iodide, a blue color is produced. (2) Ozone combines with metallic silver to form silver peroxide, which is brown. In order to detect ozone, therefore, a strip of polished silver may be exposed to the gas, and if it turns brown ozone is present.

When heated to 300° ozone loses its characteristic odor and is converted into ordinary oxygen. It thus appears that we can start with ordinary oxygen, and by means of an electric current convert it into a substance with much

more active chemical properties and differing from it so markedly that one would hardly suspect the close relation between the two; and then, further, by simply passing the active substance, or ozone, through a tube heated to 300°, it is converted back again into oxygen without loss of weight.

**Relation between Oxygen and Ozone.**—When experiment had shown that oxygen and ozone are convertible one into the other without change of weight, the suggestion was made that the difference between them might be due to a difference in the number of atoms of oxygen contained in the molecule of each. It might be, for example, that in the molecule of oxygen there are two atoms and in that of ozone three or more. If this view is correct there should be a difference between the specific gravities of the two gases, and by a study of this difference it should be possible to draw a conclusion as to the constitution of the molecule of ozone. That there is a change of volume when oxygen is changed to ozone was shown by enclosing the former in a tube constructed as shown in Fig. 5. The large part of the tube is furnished with two platinum wires which pass through the glass. By means of these
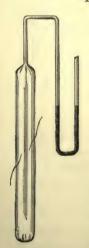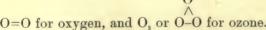


FIG. 5.

wires a silent discharge of electricity is kept up through the oxygen, and it is thus partly converted into ozone. In the smaller bent part of the tube there is a small column of concentrated sulphuric acid which serves as a stopper. Any change in the volume of the gas in the tube will cause this sulphuric acid to change its position. Now, during the conversion of the oxygen into ozone it was noticed that the volume of the gas decreased, and that, on heating the tube and thus converting the ozone into oxygen again, the original volume of the latter was restored. Unfortunately for this purpose it is not possible by any means to convert more than a comparatively small proportion of the oxygen into ozone, and it is not possible in the experiment described to de-

termine the relation between the decrease in volume and the extent of the conversion.

Certain ethereal oils, as oil of turpentine, have the power to absorb ozone without decomposing it. This fact has been taken advantage of for the purpose of determining the constitution of ozone. The method consisted in ozonizing oxygen, heating some of the mixture and measuring the increase in volume caused by conversion into oxygen; and then treating some of the same mixture with oil of turpentine, and observing the decrease in volume. By this means it is possible to calculate the change in volume which takes place when ozone is converted into oxygen. The results showed that two volumes of ozone give three volumes of oxygen, or when a given volume of oxygen is converted into ozone there is contraction to two-thirds the original volume. According to this, the molecular weight of ozone by Avogadro's law must be about 48, for from 3 volumes of oxygen there are formed 2 volumes of ozone, which, interpreted according to the molecular theory, means that three molecules of oxygen must be converted into two of ozone; but 3 molecules of oxygen weigh 96 parts; therefore, 2 molecules weighing the same, the molecular weight of ozone is 48. The further conclusion is justified that, while the molecule of ordinary oxygen consists of two atoms, that of ozone consists of three atoms. The difference may be represented by the formulas $O_2$ or

$$O=O \text{ for oxygen, and } O_3 \text{ or } O{-}O \overset{O}{\wedge} \text{ for ozone.}$$

**Ozone in the Air.**—No satisfactory evidence of the occurrence of ozone in the air has ever been furnished. Very little if anything is known in regard to the effect of ozone on the health. Larger quantities would undoubtedly act injuriously. It is commonly believed that small quantities are advantageous, as it tends to destroy substances which are unwholesome. This subject has not, however, been studied with sufficient care to justify a positive opinion in regard to it. The difficulty in drawing a conclusion is increased by the fact that there are other sub-

stances present in the air which resemble ozone in some respects, as, for example, hydrogen dioxide, $H_2O_2$ (which see).

**Allotropy.**—The occurrence of an element in two or more different modifications is called *allotropy.* Thus, ozone is called an allotropic form of oxygen. There are, however, a number of other cases of a similar kind. Phosphorus, for example, presents itself in three or four different varieties which, in some respects, differ markedly from one another. Carbon also appears in three different forms. Whether in all cases the difference between the allotropic forms of an element is due to a difference in the molecular constitution, as in the case of oxygen, is impossible to decide at present, for the reason that the molecular weights of the substances cannot always be determined. The facts learned in regard to the relations between oxygen and ozone make it appear quite probable that the explanation which holds good for this case will probably hold good for others.

**Varying Number of Atoms in the Molecules of one and the same Element.**—It has been pointed out that the molecules of hydrogen, oxygen, and some other elements consist of two atoms each. We have just seen that the molecule of ozone consists of three atoms. There are some elements which contain a different number of atoms in their molecules, according to the temperature. Thus, sulphur is a solid substance which boils at 440° C. The specific gravity of its vapor between 450° and 500° leads to the molecular weight about 192. But the atomic weight of sulphur is very nearly 32, therefore the molecule of sulphur just above its boiling-point would appear to be made up of six atoms. As the temperature is raised, the specific gravity becomes less, and above 800° it corresponds to the molecular weight 64, showing that at this high temperature the molecule apparently consists of two atoms. Above that point the specific gravity does not change materially. According to the latest investigations on this subject, it appears probable that the higher specific gravity of sulphur vapor at the

lower temperature is to be ascribed to imperfect vaporization of the substance, and that the evidence that the molecule is more complicated at lower than at higher temperature is not conclusive. Facts somewhat similar to those just mentioned have been brought to light in the case of iodine, only here the vapor at the lower temperature has a specific gravity showing that the molecule consists of two atoms, but at very high temperatures the specific gravity shows that the molecule contains only one atom. The atomic weight of mercury is the same as its molecular weight, or, in other words, the molecule and atom are in this case identical.

**Nascent State.**—One of the most curious phenomena connected with chemical action is that of the nascent state. Some elements, which under ordinary circumstances are inactive, show themselves possessed of marked activity if they are allowed to act the instant they are set free from their compounds. Thus, if carbon monoxide, CO, and ordinary oxygen are brought together at the ordinary temperature, no action takes place. If, however, carbon monoxide is brought in contact with something which easily gives off oxygen, it is converted into carbon dioxide. At ordinary temperatures, for example, chromium trioxide gives up oxygen to carbon monoxide as represented thus :

$$3CO + 2CrO_3 = 3CO_2 + Cr_2O_3.$$

So, too, hydrogen at ordinary temperatures is an inactive element, but, if brought in contact with substances the instant it is set free from a compound, it produces many marked changes. Many substances which would be left unchanged, if hydrogen were passed over them at ordinary temperatures, are changed if put in the liquid from which the hydrogen is being evolved. The most plausible explanation of facts like these is to be found in the molecular theory. Free oxygen and free hydrogen consist of molecules made up of atoms which are in combination with each other. Before these molecules can act chemically they must be broken up into atoms. When carbon

monoxide is brought together with oxygen in the molecular state, the condition is represented thus:

$$CO + O_2.$$

Before combination can take place the molecule, $O_2$, must be decomposed as represented thus:

$$O_2 = O + O ;$$

and the atoms of oxygen then combine with the carbon monoxide. Now there are some substances which yield oxygen atoms more readily than ordinary oxygen does. This is true of chromium trioxide, $CrO_3$, which in contact with substances that have the power to combine with oxygen breaks up thus:

$$2CrO_3 = Cr_2O_3 + O + O + O.$$

When hydrogen is liberated from a compound by chemical action the uncombined atoms are believed to be given off first; if there is nothing present with which the hydrogen can combine, these atoms combine with each other in pairs to form the molecules of ordinary hydrogen.

The examples furnished by allotropism and the phenomena of the nascent state show how chemical facts which otherwise appear entirely incomprehensible are satisfactorily explained by the aid of the molecular theory.

**Hydrogen Dioxide or Hydrogen Peroxide, $H_2O_2$.**—When barium dioxide is treated with hydrochloric acid or dilute sulphuric acid the reactions represented by the following equations take place:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2 ; \text{ and}$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

In the latter case the compound $BaSO_4$, or barium sulphate, is insoluble, and the liquid can easily be separated from it by filtration. If the liquid is boiled, decomposition of the hydrogen dioxide takes place, oxy-

gen being liberated and water left behind. The decomposition is represented thus :

$$2H_2O_2 = 2H_2O + O_2; \quad \text{or} \quad H_2O_2 = H_2O + O.$$

The dioxide can be obtained in the form of a colorless liquid by allowing the solution to stand in a vacuum over sulphuric acid, or by distilling its solution in a vacuum. It boils at 84°–85° under a pressure of 68 mm.

**Properties.**—Hydrogen dioxide is a clear, syrupy liquid which does not solidify at − 30°. It is characterized by marked instability. It breaks down slowly even at ordinary temperatures if simply allowed to stand. The decomposition takes place easily under the influence of heat, and if heated rapidly to 100° explosion is apt to take place. The products are water and oxygen, as indicated above. In consequence of the ease with which hydrogen dioxide gives off oxygen it is a good oxidizing agent, and it is now manufactured on the large scale for use in bleaching and in medicine, and comes into the market in solutions of different strengths. The solution has a bitter taste ; if concentrated, it affects the skin, causing a pricking sensation, and making white spots, which, however, disappear in a few hours. As hydrogen dioxide cannot be converted into vapor, its molecular weight cannot be determined by the method of Avogadro.

Determinations made by other methods, depending upon observations on the freezing-point of its solutions (see Chapter XXIII), show that its molecule is represented by the formula $H_2O_2$, and not by HO. Assuming that the formula is $H_2O_2$, what is the constitution ? We have very little clear evidence on this point, but the most prevalent view is that the atoms are connected as represented in the formula H–O–O–H, in which the oxygen atoms are in combination with each other, and also with hydrogen. The principal ground upon which this conception rests is that this is the only way in which two hydrogen atoms and two oxygen atoms can be joined to-

gether, if the oxygen atoms are bivalent and the hydrogen atoms univalent. This, clearly, is not good evidence, as it is quite possible that oxygen may not be bivalent in this compound. Indeed, there are some facts which seem to show pretty conclusively that the oxygen atoms are quadrivalent, and that the constitution of hydrogen dioxide should be represented by the formula

$$H–O \equiv O–H.$$

It is impossible here to discuss the significance of this formula. Suffice it to say that it is largely based upon the results of observations on the refractive power of the compound.

**Occurrence in the Air.**—That hydrogen dioxide occurs in the air has already been stated. It is also found in rain and snow. The quantity in the air is extremely small, and it varies at different times of the day, the action of sunlight being evidently favorable to its formation.

**Characteristic Reactions.**—Like ozone, hydrogen dioxide decomposes potassium iodide, setting iodine free :

$$H_2O_2 + 2KI = 2KOH + I_2.$$

This fact may be utilized for the purpose of detecting the compound. The separation of the iodine does not take place readily as in the case of ozone, but the action is hastened by the addition of a very small quantity of a dilute solution of ferrous sulphate, $FeSO_4$.—An acid solution of potassium permanganate is decolorized by hydrogen dioxide.—If in a glass cylinder a layer of ether is poured upon a solution of hydrogen dioxide and a drop of a solution of potassium dichromate is then added, and the cylinder thoroughly shaken, the ether will take up a blue compound, and will itself become blue.

When hydrogen dioxide is brought together with substances which give up oxygen readily, action generally takes place involving decomposition of the hydrogen dioxide as well as of the other substance. Thus, when

it is brought together with silver oxide, $Ag_2O$, this reaction takes place :

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

So, also, it undergoes decomposition with ozone as represented thus :

$$O_3 + H_2O_2 = H_2O + 2O_2.$$

The explanation of these facts is to be found partly in the attraction of the atoms of oxygen for each other. In the molecule of silver oxide and of hydrogen dioxide there is an atom of oxygen which is held loosely. When the substances are brought together these loosely combined atoms attract and combine with each other, as may be represented thus :

$$(O_2)O + O(H_2O) = O_2 + O_2 + H_2O.$$

**Thermochemical Considerations.**—By methods which need not be described here, it has been determined that when ozone is converted into oxygen heat is evolved, and the thermochemical equation expressing the facts is this :

$$2O_3 = 3O_2 = + 2 \times 36,200 \text{ cal.}$$

In accordance with the explanation given on page 37, this means that when two molecules of ozone are converted into three molecules of oxygen 72,400 c. are evolved. So, also, when oxygen is converted into ozone heat is absorbed, the equation being

$$(O_2, O) = O_3 = - 36,200 \text{ cal.}$$

To convert oxygen into ozone therefore requires an addition of energy. A reaction which requires an addition of heat is called an *endothermic* reaction, and one which takes place with an evolution of heat is called an *exothermic* reaction. In general, that exothermic reaction which is accompanied by the greatest evolution of heat takes place most readily, and endothermic reactions do not take place without the addition of energy from with-

out. In the language of physics, we say that ozone contains more energy than oxygen, and therefore it acts more readily.

Somewhat similar relations are observed between hydrogen dioxide and water. The decomposition of the dioxide into water and oxygen is accompanied by an evolution of heat:

$$H_2O_2 = H_2O + O = + 23,100 \text{ cal.};$$

and the formation of the dioxide requires the addition of the same amount of heat:

$$(H_2O, O) = - 23,100 \text{ cal.}$$

In order to get the dioxide, therefore, the reaction must be of such a character as to furnish this amount of heat. In the action of hydrochloric acid upon barium dioxide there is more heat evolved than is required in the formation of hydrogen dioxide, and therefore the formation in this way is possible.

# CHAPTER VIII.

## CHLORINE—HYDROCHLORIC ACID.

**Historical.**—Sodium chloride or common salt, which is the principal chlorine compound found in nature, has been known for a very long time. In 1774 Scheele first called attention to chlorine in his treatise on the black oxide of manganese or manganese dioxide. In accordance with the ideas then prevailing, he called it dephlogisticated muriatic acid. Berthollet suggested in 1785 that it was oxidized hydrochloric acid, and it was then regarded as consisting of the hypothetical element, *murium*, in combination with oxygen. In 1810 Davy pointed out that the idea, previously expressed by Gay-Lussac and Thénard, that the substance is an element, is in the highest degree probable, and he gave it the name chlorine (from χλωρός, greenish-yellow). Since that time everything learned in regard to chlorine has gone to show that it is an element.

**Occurrence of Chlorine.**—Though widely distributed in nature, chlorine never occurs in the uncombined state, for the reason that it combines with other substances with great ease, and, if it were set free, it would at once enter into combination. It does not occur in very large quantity as compared with oxygen and hydrogen. It is found chiefly in combination with the element sodium as common salt, or sodium chloride, a compound of the composition represented by the formula NaCl. It is also found in combination with other elements, as potassium, magnesium, etc., as in the celebrated mines at Stassfurt, Germany. In comparatively small quantity it occurs in combination with silver, forming one of the most valuable silver ores. All the chlorine which we have to deal with is made from common salt.

**Preparation.**—The problem to be solved in the preparation of chlorine from common salt is the separation of the two elements sodium and chlorine. This cannot be accomplished directly as the separation of mercury and oxygen in the decomposition of mercuric oxide, $HgO$, and there is no easily obtained compound which gives off chlorine when heated. The method adopted consists in making hydrochloric acid, $HCl$, from sodium chloride, and then treating this acid with some substance which readily gives off oxygen. The change of sodium chloride to hydrochloric acid is readily accomplished by treating salt with ordinary sulphuric acid—a reaction carried on on the large scale in the manufacture of sodium carbonate or "soda." When the two are brought together a change takes place which will be studied more in detail farther on. The reaction is represented by the equation

$$(1) \quad 2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

<div style="text-align:center">Sodium     Sulphuric     Sodium     Hydrochloric<br>chloride     acid     sulphate     acid</div>

As will be seen, the sodium of the sodium chloride and the hydrogen of the sulphuric acid exchange places—a kind of action which is quite common.

The decomposition of the hydrochloric acid and liberation of chlorine under the influence of oxygen takes place as represented in this equation :

$$(2) \quad 2HCl + O = H_2O + Cl_2.$$

As there is an unlimited supply of oxygen in the air, it would be advantageous if the decomposition of the hydrochloric acid could be effected by means of the element in the free state. But free oxygen alone will not accomplish the change. A process has been invented, however, for the manufacture of chlorine on the large scale which depends upon the decomposition of hydrochloric acid by the oxygen of the air. This is Deacon's process. It consists in passing hydrochloric acid and air together through a heated tube containing clay balls saturated with a solution of copper sulphate, and then dried. If

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the temperature of the tube is not raised too high the copper sulphate remains unchanged. Exactly why the oxidation of the hydrochloric acid takes place under these circumstances is not positively known, but it probably depends upon the formation and decomposition of intermediate products. Deacon's process is used quite extensively on the continent of Europe, while in England and Scotland another method, apparently more complicated, known as Weldon's process, is chiefly used. In the laboratory chlorine is generally made by treating hydrochloric acid with manganese dioxide. The reaction is represented thus :

$$(1) \quad MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

This is explained by the tendency of hydrogen to combine with oxygen to form water. When the compound MnO is treated with hydrochloric acid, this reaction takes place :

$$MnO + 2HCl = MnCl_2 + H_2O.$$

In this case there is a simple exchange of places by the manganese and hydrogen and the oxygen and chlorine, the great affinity of hydrogen for oxygen being a prominent cause of the change.

So, also, when manganese dioxide is treated with hydrochloric · acid, the oxygen may be first replaced by chlorine, as represented in the equation

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

But the compound $MnCl_4$ gives up half its chlorine when heated :

$$MnCl_4 = MnCl_2 + Cl_2 \, ;$$

so that the action of hydrochloric acid on manganese dioxide is represented by the equation (1) above. Some recent investigations make it appear probable that the reaction is more complicated than it is here represented to be; that the first product of the action of hydrochloric acid on manganese dioxide is a compound

of the composition $H_2MnCl_6$ (or $H_2MnCl_5$); and that this breaks down under the influence of heat thus:

$$H_2MnCl_6 = MnCl_2 + 2HCl + Cl_2.$$

These reactions will be taken up under the head of Manganese (which see).

Instead of making hydrochloric acid from salt, and then treating it with manganese dioxide, it is better to mix the manganese dioxide and common salt together, and pour upon the mixture the necessary quantity of sulphuric acid. In this case the manganese dioxide and sulphuric acid give off oxygen, and the common salt and sulphuric acid give off hydrochloric acid. The oxygen then oxidizes the hydrochloric acid, and chlorine is liberated. At least this is a probable explanation of the reaction, for it is known that when manganese dioxide is heated with sulphuric acid oxygen is liberated, as represented in the equation

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

**Weldon's Process.**—As there is a large demand for chlorine, much attention has been given to the improvement of the methods for its preparation. One of the objections to the ordinary method is the comparatively high price of the mineral, manganese dioxide. As this is converted into the chloride, $MnCl_2$, in the preparation of chlorine, and the chloride is of no value, the expense of preparation is quite high. A process has been invented for the regeneration of the manganous chloride, $MnCl_2$, or for the conversion of this compound into an oxygen compound which with hydrochloric acid will give chlorine. This is Weldon's process. It will be taken up under the head of Manganese (which see).

**Electrolytic Process.**—Various processes have been devised for the preparation of chlorine by the action of an electric current on a solution of sodium chloride or of hydrochloric acid. Such electrolytic processes are now in use, and by means of them the price of chlorine has been much lowered.

**Properties.**—Chlorine is a greenish-yellow gas. It has

a disagreeable odor, and acts upon the membranes lining the throat and nose, causing irritation and inflammation, suggesting a "cold in the head." Inhaled in concentrated form it causes death. Its specific gravity at 20° is 2.48 (air = 1), and as compared with hydrogen it is 35.18. A liter of chlorine gas, under standard conditions, weighs 3.162 grams. It is soluble in water and acts upon mercury, and therefore cannot be collected by displacement of either of these liquids. The most convenient way to collect it is by displacement of air. It can also be collected over warm water in which it is less soluble than in cold water, or over a saturated solution of sodium chloride in which it is but slightly soluble. It is easily compressed to a liquid, and is now sold in this form in cast-iron cylinders.

It is a remarkably active substance, combining with or acting in some way upon most other substances even at ordinary temperature. This activity may be illustrated by introducing into vessels containing chlorine a little finely powdered antimony, a few pieces of thin copper-foil, a piece of paper with ink-marks on it, some flowers, and pieces of cotton-prints. The antimony will take fire and a white substance will be formed. The reaction is represented by the following equation:

$$Sb + 3Cl = SbCl_3.$$

The copper-foil also takes fire, and is converted into a chloride as represented thus:

$$Cu + 2Cl = CuCl_2.$$

Many other substances unite directly with chlorine with evolution of heat and light, and form compounds which are called *chlorides*. This kind of action is of the same character as that which takes place in oxygen. There is, however, this difference between reactions in oxygen and in chlorine: the latter frequently take place at ordinary temperatures, whereas those in oxygen require an elevation of temperature to start them. In both cases the gases combine with the other

substances directly, and disappear as such, and the light and heat are caused by the act of combination.

Dry liquid chlorine, at its boiling temperature $(-33°.6)$ does not act on potassium, sodium, or aluminium.

The action of chlorine upon ink, flowers, and cotton-print illustrates its power to *bleach*. It is important to notice that if the colored objects be introduced dry into dry chlorine the action does not take place. Moisture is generally essential to the bleaching by chlorine. Chlorine acts directly upon some dye-stuffs, converting them into colorless substances. In other cases it has been shown that the destruction of the color is due to the action of oxygen, which is set free from water by chlorine. In direct sunlight chlorine decomposes water according to the equation

$$H_2O + Cl_2 = 2HCl + O.$$

This decomposition can be illustrated by filling a long tube with a solution of chlorine in water, and inverting it in a shallow vessel containing some of the same solution. If this is placed in the direct sunlight, bubbles of gas will be seen to rise in the tube and these will collect at the top, while the color of the solution, which was at first greenish-yellow like that of chlorine, will disappear. The gas which collects in the upper part of the tube is oxygen.

The disintegrating action of chlorine upon substances of animal and vegetable origin may be illustrated by moistening a piece of filter-paper with some oil of turpentine, and introducing it into a vessel of chlorine. A flash of light is seen, and a dense black cloud is formed. The black substance is mainly carbon. Oil of turpentine is a compound of carbon and hydrogen. Chlorine abstracts the hydrogen from the carbon, leaving the latter mainly in the uncombined state. If the chlorine is allowed to act slowly upon the oil of turpentine and similar organic substances, the chlorine is substituted atom for atom for the hydrogen, and a series of so-called substitution-products is obtained.

Chlorine dissolves readily in water and forms a solution known as chlorine water. It has the odor and color of the gas, and it is frequently used in the laboratory instead of the gas. From what has been said it is evident that it must be kept protected from the sunlight, or decomposition will take place, resulting in the formation of hydrochloric acid and oxygen.

**Different Kinds of Action.**—A careful study of the different kinds of action exhibited by chlorine shows that they may be classified under three heads :

(1) First it acts by direct combination with elements as in the experiments with antimony and copper, and, as will be shown, with hydrogen and many other elements. Just as the compounds of oxygen with other elements are called oxides, so the compounds of chlorine with other elements are called *chlorides*. Thus the compound of antimony and chlorine, $SbCl_3$, is called antimony chloride ; that of zinc and chlorine, $ZnCl_2$, is called zinc chloride ; etc. In case an element forms more than one compound with chlorine, the names used to distinguish between them are similar to those used for oxides. Mercury forms two chlorides which have the composition represented by the formulas $HgCl$ and $HgCl_2$. The one with the smaller proportion of chlorine is called *mercurous chloride*, and the one with the larger proportion of chlorine is called *mercuric chloride*. So, too, there are two chlorides of iron which correspond to the formulas $FeCl_2$ and $FeCl_3$. The former is called *ferrous chloride*, and the latter *ferric chloride.*

(2) The second kind of action of chlorine is that which is called substitution. This was referred to in connection with the action of chlorine on the oil of turpentine. The general character of this kind of action may be explained by the aid of the following example. There is an important compound of carbon and hydrogen called benzene, which has the formula $C_6H_6$. When chlorine is passed through this compound, which is a liquid, a gas is given off which can easily be shown to be hydrochloric acid, $HCl$. This action continues until there is no hydrogen left in combination with the carbon, but in

place of the benzene there is now a compound of the formula $C_6Cl_6$. This has been shown to be the final product of a series of reactions represented by the following equations:

$$C_6H_6 \quad + Cl_2 = C_6H_5Cl + HCl;$$
$$C_6H_5Cl + Cl_2 = C_6H_4Cl_2 + HCl;$$
$$C_6H_4Cl_2 + Cl_2 = C_6H_3Cl_3 + HCl;$$
$$C_6H_3Cl_3 + Cl_2 = C_6H_2Cl_4 + HCl;$$
$$C_6H_2Cl_4 + Cl_2 = C_6HCl_5 + HCl;$$
$$C_6HCl_5 + Cl_2 = C_6Cl_6 \quad + HCl.$$

In each stage one atom of chlorine is substituted for an atom of hydrogen, but the hydrogen does not escape as such. It combines with chlorine and passes off in the form of hydrochloric acid.

(3) The third kind of action is that noticed in bleaching, which depends upon the decomposition of water and the escape of oxygen as already explained. This action does not take place in the dark, but does take place readily in the direct sunlight. We have, however, seen that when oxygen acts upon hydrochloric acid under proper conditions water is formed and chlorine set free. It appears, therefore, that, under some circumstances, this reaction is possible:

$$2HCl + O = H_2O + Cl_2;$$

and, under other circumstances, this one:

$$H_2O + Cl_2 = 2HCl + O.$$

These facts appear to be contradictory. What part the sunlight plays is not known, though it is well known that it is capable of producing a great variety of chemical changes. We shall soon see that it is only necessary to allow it to act for an instant upon a mixture of hydrogen and chlorine to cause them to combine with violence. Then, too, the various processes known under the general name of photography depend upon chemical changes brought about by the sunlight. Leaving out of consideration this kind of action, the decomposition of hydrochloric acid by oxygen and that of water by chlorine can

be explained by a consideration of the heat relations. The heat evolved in the formation of 1 molecule of water in the gaseous form is 58,069 cal., while that absorbed in the decomposition of 2 molecules of hydrochloric acid is 44,002 cal. Therefore, the reaction,

$$2HCl + O = H_2O + Cl_2,$$

is accompanied by an evolution of heat. It is exothermic, and can take place without the addition of energy from without. If water is formed as a liquid, the heat evolved for 1 molecule is 68,357 cal., while that evolved by the formation of 2 molecules of hydrochloric acid in solution is 78,630 cal. Therefore, the heat evolved in the formation of hydrochloric acid in solution is greater than that required to decompose water, and this reaction takes place. This does not, however, explain what part the sunlight plays in the process.

**Chlorine Hydrate and Liquid Chlorine.** — When chlorine gas is passed into water cooled down almost to the freezing-point, crystals appear in the vessel. These consist of chlorine and water as represented by the formula $Cl + 5H_2O$; or, assuming that it is formed by the combination of the molecules of chlorine with water, the formula should be written $Cl_2 + 10H_2O$. It gives off chlorine at the ordinary temperature and, if allowed to stand, undergoes complete decomposition into chlorine and water. If gently heated the chlorine is given off rapidly. This fact was taken advantage of by Faraday for the purpose of subjecting the gas to high pressure and low temperature. For this purpose he placed some of the hydrate in a strong glass tube of the form represented in Fig. 6. The compound was put in the part of the tube marked *ab*, and the other end, *c*, then sealed. The arm *ab* was warmed by dipping it in warm water, while the other arm was placed in a freezing mixture. Under these circumstances the chlorine is given off from the hydrate, but being unable to escape from the tube the



FIG. 6.

pressure is increased to such an extent that at the low temperature the gas assumes the liquid form.

**Applications of Chlorine.**—Chlorine is used very extensively in the arts, particularly for the purpose of bleaching. It is also used for the manufacture of a large number of compounds which contain chlorine, the principal ones being bleaching powder or calcium hypochlorite, and potassium chlorate. If used in sufficient quantity chlorine is an excellent disinfectant and deodorizer. By far the largest quantity of the chlorine manufactured is converted into bleaching powder or calcium hypochlorite, as this can be conveniently transported, and the chlorine can be obtained from it when desired. It is only necessary to expose it to the air to effect a partial decomposition accompanied by a liberation of chlorine ; and the addition of hydrochloric or sulphuric acid causes it to give it up completely, as will be shown farther on. This bleaching powder is now used almost exclusively instead of chlorine gas for bleaching.

## HYDROCHLORIC ACID.

**Historical.**—Hydrochloric acid was first prepared in large quantity by Glauber in the seventeenth century, and his description is not unlike those which one frequently reads nowadays referring to some patent medicine. The method of preparation used by him was the same as that used at present, *viz.*, the action of sulphuric acid upon common salt.

**Study of the Action of Hydrogen upon Chlorine.**—If hydrogen and chlorine are brought together in the dark no action takes place, no matter how long they are allowed to stand together. If, however, the mixture is put in diffused sunlight, gradual combination takes place ; and if the direct light of the sun is allowed to shine for an instant on the mixture, explosion occurs, and this is the sign of the combination of the two gases. The same sudden combination is effected by applying a flame or spark to the mixture, or by illuminating it in-

stantaneously with the light from burning magnesium
or an electric light.   On comparing these facts with
those learned in studying the action of hydrogen on
oxygen a marked difference is evident.   Hydrogen and
oxygen do not combine either in the dark or the direct
sunlight, but only when a spark is brought in contact
with the mixture.

Another way in which hydrogen can be made to
combine with chlorine is by introducing a jet of burning
hydrogen into a vessel containing chlorine.   The hydro-
gen will continue to burn, but the character of the flame
will change completely, and above the vessel white
fumes will be observed.   This burning of hydrogen in
chlorine is entirely analogous to the burning of hydro-
gen in oxygen.   It is simply an act of combination of
the two gases, in each case, accompanied by an evolution
of light and heat.   And just as oxygen can be burned in
hydrogen by a proper arrangement of apparatus, so
chlorine can also be burned in hydrogen.

To determine the relation between the volumes of hy-
drogen and chlorine which combine with each other and
the volume of the product formed is more difficult than
in the case of hydrogen and oxygen, mainly for the rea-
son that chlorine acts upon mercury and is dissolved by
water.   It is necessary to proceed indirectly.

Instead of causing hydrogen and chlorine to combine,
hydrochloric acid is decomposed and the volumes of the
hydrogen and chlorine obtained are determined.   One
method of effecting this consists in decomposing hydro-
chloric acid by an electric current in an apparatus
like that referred to in connection with the decom-
position of water.   As chlorine is, however, soluble
in water, the apparatus is filled with a saturated solution
of common salt to which a strong solution of hydro-
chloric acid in water is added.   On passing a fairly
strong current, the hydrochloric acid is decomposed,
hydrogen being given off at one pole and chlorine at
the other.   For a given volume of hydrogen the same
volume of chlorine is liberated, which makes it ap-
pear probable that hydrogen and chlorine are combined

in hydrochloric acid in the proportion of volume to volume.

For the purpose of further studying the volume relations, the following experiment is of value. A tube is filled with hydrochloric acid gas. A small piece of potassium is then introduced, when decomposition takes place as represented in the equation

$$K + HCl = KCl + H.$$

The gas left in the vessel is hydrogen, as can easily be shown. On measuring its volume it is found to be just half that of the hydrochloric acid gas decomposed. Taking this fact into consideration with the fact that whenever hydrochloric acid is decomposed by an electric current equal volumes of hydrogen and chlorine are obtained, it appears that in the formation of hydrochloric acid gas 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid, a fact which was referred to in the chapter on the Atomic Theory. The weight of the hydrogen is found to bear to the weight of the hydrochloric acid the proportion 1 : 36.18. In other words, in 36.18 parts of hydrochloric acid there are 35.18 parts of chlorine and 1 part of hydrogen.

**Preparation.**—For the preparation of hydrochloric acid in the laboratory as well as on the large scale, ordinary sulphuric acid is poured upon common salt. Two reactions may take place between these substances, depending largely upon the amount of sulphuric acid used. If the two substances are brought together in the proportion of the weights of their molecules or their molecular weights, the principal reaction is the one represented in the following equation :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

In this case the atom of sodium of the molecule of sodium chloride is substituted for one atom of hydrogen in the molecule of sulphuric acid, while the hydrogen and chlorine unite to form hydrochloric acid. If, on the other hand, the substances are brought together in the

proportion of 2 molecules of sodium chloride and 1 molecule of sulphuric acid the principal reaction is the following:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

**Properties.**—Hydrochloric acid is a colorless transparent gas, and has a sharp penetrating taste and smell. Inhaled it produces suffocation. It is extremely easily soluble in water, 1 volume of water at ordinary temperatures dissolving 450 times its own volume of the gas, and at 0°, 500 times. The solution of the gas in water is what is generally called hydrochloric acid. So great is the attraction of the gas for water that it condenses moisture from the air; hence, although the gas itself is quite colorless and transparent, when it comes in contact with the air dense white clouds are formed, which are not formed if it is kept from contact with the air, as can easily be shown by filling glass vessels with the gas. Hydrochloric acid does not burn and does not support combustion. This is equivalent to saying that it does not combine with oxygen under ordinary circumstances, and that substances which combine with the oxygen of the air do not combine with hydrochloric acid. On the other hand, we have seen that under some circumstances oxygen does act upon hydrochloric acid and cause an evolution of chlorine. The gas is comparatively easily condensed to the liquid form.

When a concentrated solution of hydrochloric acid in water is heated, gas is given off, but if a dilute solution is heated water is given off. In either case, when the composition of the liquid is that represented by the formula $HCl + 8H_2O$, it boils under the ordinary pressure of the atmosphere unchanged. If the pressure is lowered the composition of the liquid which passes over in the process of distillation changes, so that it contains a larger percentage of hydrochloric acid the lower the pressure becomes. This fact seems to show that the liquid of the composition $HCl + 8H_2O$, which boils unchanged at the temperature 110° under the ordinary pressure of the atmosphere is not a chemical compound.

On the other hand, it certainly does not conduct itself like most ordinary solutions of gases.

There is a definite compound of hydrochloric acid with water called *hydrochloric acid hydrate*, which has the composition $HCl + 2H_2O$. This is formed by passing hydrochloric acid gas into the concentrated aqueous solution cooled down to $-22°$. Under these circumstances the hydrate separates in the form of crystals.

*Commercial hydrochloric acid* is a yellowish liquid, the color being due to the presence of impurities, such as iron and organic substances. The solution is obtained in the factories in which "soda" or sodium carbonate is made. This is an extremely important substance in the arts. It does not occur in nature, but is manufactured from common salt. In the process most commonly used salt is first converted into sodium sulphate, $Na_2SO_4$, by treating it with sulphuric acid. Hydrochloric acid is necessarily given off. When the factories were first established in England, the gas was allowed to escape as a waste product, but the effects produced by it upon the vegetation of the surrounding country were so injurious that a law was passed prohibiting the manufacturers from allowing the gas to escape. It is now collected by causing it to pass through towers so constructed as to expose a large surface of bricks or sandstone plates over which a current of cold water is constantly kept flowing. This water dissolves the hydrochloric acid, and the solution collected below is commercial hydrochloric acid. In this way enormous quantities of the acid are produced, but its uses are numerous and it always commands a price.

*Pure hydrochloric acid* is a solution of the pure gas in pure water. It is colorless, and when concentrated it gives off fumes when exposed to the air. The solution when heated gives off a large part of the gas contained in it, and by boiling it can all be evaporated.

**Chemical Action of Hydrochloric Acid.**—If the action of hydrochloric acid towards the elements should be studied systematically it would be found that many of them act by simply taking the place of the hydrogen, as has

already been illustrated in the preparation of hydrogen by treating hydrochloric acid with zinc when this reaction takes place :

$$Zn + 2HCl = ZnCl_2 + H_2.$$

With iron the reaction is :

$$Fe + 2HCl = FeCl_2 + H_2;$$

with tin :

$$Sn + 2HCl = SnCl_2 + H_2;$$

with potassium :

$$K + HCl = KCl + H, \text{ or}$$
$$K_2 + 2HCl = 2KCl + H_2;$$

with sodium :

$$Na_2 + 2HCl = 2NaCl + H_2;$$

with calcium :

$$Ca + 2HCl = CaCl_2 + H_2; \text{ etc., etc.}$$

On the other hand, there are many elements which do not act in this way towards hydrochloric acid. Sulphur, nitrogen, phosphorus, carbon, and boron may be taken as examples. These elements do not act upon hydrochloric acid at all. We might, therefore, divide the elements into two classes : (1) those which act upon hydrochloric acid setting hydrogen free and forming chlorides ; and (2) those which do not act upon hydrochloric acid.

Again, when hydrochloric acid acts upon the oxides of those elements which have the power to liberate hydrogen from it, it forms the same chlorides as are formed when the element alone acts, but instead of hydrogen being liberated water is formed. Thus when the acid acts upon zinc oxide, ZnO, the reaction takes place thus :

$$ZnO + 2HCl = ZnCl_2 + H_2O;$$

with lime or calcium oxide, CaO, it is :

$$CaO + 2HCl = CaCl_2 + H_2O ;$$

with potassium oxide :

$$K_2O + 2HCl = 2KCl + H_2O ; \text{ etc., etc.}$$

In these reactions there are two forces at work tending to effect the change. There is, first, the affinity of the element, which is combined with oxygen, for chlorine, and, second, the affinity of the hydrogen for oxygen. We should, therefore, naturally expect hydrochloric acid to act more readily upon the oxides than upon elements, and it has been found that this is the case.

If the so-called hydroxides of those elements which act upon hydrochloric acid be brought in contact with the acid, action takes place even more readily than with the oxides, and the products are the same. Thus potassium hydroxide and hydrochloric acid give potassium chloride and water :

$$KOH + HCl = KCl + H_2O ;$$

calcium hydroxide and hydrochloric acid give calcium chloride and water, thus :

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O ;$$

aluminium hydroxide and hydrochloric acid give aluminium chloride and water, thus :

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O ; \text{ etc., etc.}$$

There are then elements which act upon hydrochloric acid liberating hydrogen and forming chlorides ; and the oxides and hydroxides of these elements act upon hydrochloric acid forming chlorides and water. The elements which act in this way are commonly called *metals* or, for reasons which will be discussed farther on, *base-forming elements.*

If those elements which do not set hydrogen free from

hydrochloric acid are treated directly with chlorine, they generally combine with it to form chlorides. But these chlorides differ markedly from the chlorides of the metals, especially in their conduct towards water. Two examples will suffice for the present. Phosphorus forms a chloride of the formula $PCl_3$, known as phosphorus trichloride. In contact with water it undergoes decomposition according to this equation :

$$PCl_3 + 3H_2O = PO_3H_3 + 3HCl ;$$

so, too, the chloride of boron, $BCl_3$, undergoes the same kind of change :

$$BCl_3 + 3H_2O = BO_3H_3 + 3HCl.$$

Similarly, the other chlorides of the elements of this class tend to pass into the oxides or hydroxides when brought in contact with water. Those elements which do not act upon hydrochloric acid setting hydrogen free and forming chlorides are generally called *non-metals* or, for reasons which will appear later, *acid-forming elements.* The chlorides of the acid-forming elements are generally decomposed by water and the corresponding oxides or hydroxides are formed. In general terms, the oxide of a base-forming element or of a metal is acted upon by hydrochoric acid, a chloride and water being formed ; and the chloride of an acid-forming element or of a nonmetal is acted upon by water, a hydroxide, or oxide, and hydrochloric acid being formed. We shall have many illustrations of the opposite chemical character of these two classes of elements, and we shall see that many of the most important and characteristic chemical reactions are associated with these differences.

# CHAPTER IX.

## COMPOUNDS OF CHLORINE WITH OXYGEN AND WITH HYDROGEN AND OXYGEN.

**General.**—As has been seen, chlorine combines very readily with hydrogen, and hydrogen with oxygen, and the products are stable compounds. On the other hand, chlorine cannot be made to combine directly with oxygen. By indirect processes they can be combined, but the compounds undergo decomposition easily, yielding back the chlorine and oxygen contained in them. Before taking up the compounds of chlorine and oxygen, however, it will be best to discuss, as far as may be necessary, the compounds of chlorine, hydrogen, and oxygen which are more easily made, and from which the oxides are made.

**Principal Reactions for making Compounds of Chlorine with Hydrogen and Oxygen.**—One of the principal reactions made use of for the preparation of compounds of chlorine, oxygen, and hydrogen consists in treating potassium hydroxide with chlorine. The strong affinity of chlorine for potassium shown by the decomposition of hydrochloric acid by potassium would lead us to expect that when chlorine acts upon potassium hydroxide, potassium chloride, KCl, would be formed:

$$KOH + Cl = KCl + O + H.$$

But it also has a strong affinity for hydrogen, so that hydrochloric acid would be formed as well as potassium chloride:

$$KOH + 2Cl = KCl + HCl + O.$$

The oxygen can, however, combine with potassium chloride and form compounds, $KClO$, $KClO_2$, $KClO_3$, and

$KClO_4$; and hydrochloric acid, if formed, would combine with potassium hydroxide, thus :

$$KOH + HCl = KCl + H_2O.$$

When potassium hydroxide is treated with chlorine we may therefore expect to obtain potassium chloride, $KCl$; some compound containing potassium, chlorine, and oxygen; and water. Experiment has shown that the action takes place as we should expect, and that the compound of potassium, chlorine, and oxygen is different according to the conditions of the experiment. If the solution of caustic potash is warm and concentrated the product is richer in oxygen than when the solution is dilute and cold. With the concentrated solution the reaction takes place thus :

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

While five atoms of potassium appear in the form of the chloride, one appears in the form of an oxygen compound, $KClO_3$, *potassium chlorate*, which we have already had to deal with in connection with the preparation of oxygen. With the dilute solution of caustic potash the reaction takes place thus :

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

The oxygen product in this case is *potassium hypochlorite*, $KClO$.

*Potassium chlorate*, $KClO_3$, and *potassium hypochlorite*, $KClO$, bear the same relation to two compounds, $HClO_3$ and $HClO$, that potassium chloride, $KCl$, and sodium chloride, $NaCl$, bear to hydrochloric acid. But we have seen that hydrochloric acid can easily be obtained from sodium chloride by treating it with sulphuric acid. Potassium chloride undergoes the same change when treated with sulphuric acid. Indeed, we shall see that nearly all compounds containing sodium or potassium give up these metals when treated with sulphuric acid, and take up hydrogen in the place of them.

Treating potassium chloride with sulphuric acid this reaction takes place :

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$

Similarly, treating potassium chlorate with sulphuric acid, this reaction takes place :

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3.$$

The compound $HClO_3$ is called *chloric acid.* Further, when potassium hypochlorite is decomposed by sulphuric acid under proper circumstances, it undergoes the same kind of decomposition :

$$2KClO + H_2SO_4 = K_2SO_4 + 2HClO.$$

The compound $HClO$ is called *hypochlorous acid.*

**Chloric Acid, $HClO_3$.**—The preparation of chloric acid from potassium chlorate is accomplished by treating a water solution of the chlorate with fluosilicic acid, $H_2SiF_6$, with which potassium forms an insoluble compound. The reaction which takes place is represented thus :

$$2KClO_3 + H_2SiF_6 = K_2SiF_6 + 2HClO_3.$$

The compound $K_2SiF_6$ is known as potassium fluosilicate. It will be observed that this reaction is of the same general character as that represented above as taking place between potassium chlorate and sulphuric acid. The difference between the two reactions is that potassium fluosilicate is insoluble in water, while potassium sulphate is soluble. By using fluosilicic acid, therefore, a solution of chloric acid is obtained free from other substances, provided just enough of the fluosilicic acid is added to form potassium fluosilicate with all the potassium. This solution is unstable, and if heated above 40° the chloric acid undergoes decomposition according to the equation

$$4HClO_3 = Cl_2 + 3O + 2HClO_4 + H_2O.$$

**Properties.**—Chloric acid acts upon metals in the same general way that hydrochloric acid does. It gives up its hydrogen and takes up metal in its place forming compounds like potassium chlorate, $KClO_3$, sodium chlorate, $NaClO_3$, etc. In consequence of the ease with which it gives up oxygen, it is used extensively for the preparation of oxygen, and for the purpose of adding oxygen to other substances, or as an oxidizing agent. Potassium chlorate and other compounds of similar character derived from chloric acid are used in the manufacture of fire-works.*

**Hypochlorous Acid, HClO.**—The formation of potassium hypochlorite, KClO, by treating caustic potash with chlorine has been mentioned. A similar reaction is employed on the large scale in the manufacture of bleaching powder or "chloride of lime." This consists in treating slaked lime or calcium hydroxide with chlorine. The action is represented thus:

$$2Ca\,(OH)_2 + 2Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O.$$

The compound $Ca(ClO)_2$ known as calcium hypochlorite is derived from hypochlorous acid by replacing two atoms of hydrogen in two molecules of the acid by one atom of the bivalent metal calcium

$$\begin{matrix} HClO \\ HClO \end{matrix} \text{ gives } Ca\begin{pmatrix} ClO \\ ClO \end{pmatrix} \text{ or } Ca(ClO)_2.$$

Just as a mixture of potassium chloride and potassium hypochlorite is formed when potassium hydroxide is used, so apparently a mixture of calcium chloride and calcium hypochlorite is formed when calcium hydroxide is used. This point will be discussed to some extent under the head of Calcium Hypochlorite (which see), when it will be shown that there are good reasons for

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* Great care is necessary when working with potassium chlorate, as with many substances it forms explosive mixtures. Treated with concentrated acids it undergoes rapid and violent decomposition.

believing that the product called bleaching powder is a distinct chemical compound and not a mixture of the chloride and hypochlorite. For our present purpose, however, it may be considered as such a mixture, for under most circumstances it acts as if it were. When treated with sulphuric acid or hydrochloric acid, bleaching powder gives up hypochlorous acid first, and then chlorine. The character of the action will be clear by considering first the conduct of the corresponding potassium compounds. When a mixture of potassium hypochlorite and potassium chloride is treated with dilute sulphuric acid, the hypochlorite is decomposed with liberation of hypochlorous acid and formation of potassium sulphate :

$$2KClO + H_2SO_4 = K_2SO_4 + 2HClO.$$

At the same time the sulphuric acid acts upon the chloride liberating hydrochloric acid :

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$

But when hydrochloric acid and hypochlorous acid are brought together they react as represented in this equation :

$$HClO + HCl = H_2O + Cl_2.$$

So that the result of treating a mixture of hypochlorite and chloride with sulphuric acid is the liberation of chlorine :

$$KClO + KCl + H_2SO_4 = K_2SO_4 + H_2O + Cl_2.$$

With bleaching powder the reaction is :

$$Ca(ClO)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 2Cl_2.$$

Hypochlorous acid can also be made by passing chlorine gas into water in which mercury oxide is suspended. The reaction is :

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HOCl.$$

The concentrated solution of hypochlorous acid has a peculiar odor suggesting that of chlorine. It is the odor which is familiar as that of bleaching powder or chloride of lime. The acid undergoes decomposition very readily, forming chlorine and a compound of chlorine and oxygen. A solution of the acid bleaches about as well as chlorine, and when bleaching powder is used for bleaching it is largely the hypochlorous acid set free from the hypochlorite which effects the desired changes.

Like chloric acid, hypochlorous acid is an excellent oxidizing agent, and is used in the laboratory in this capacity.

**Chlorous Acid, $HClO_2$.**—Although a substance of this composition is not known, a number of compounds have been made which are closely related to it. Such, for example, are the compounds potassium chlorite, $KClO_2$, silver chlorite, $AgClO_2$, etc. Potassium chlorite is formed when a solution of chlorine dioxide, $ClO_2$, in water is treated with a solution of potassium hydroxide. From the solution of the potassium compound, the silver compound can be made by adding a solution of silver nitrate.

**Perchloric Acid, $HClO_4$.**—When the preparation of oxygen by heating potassium chlorate was considered, it was pointed out that in the first stage of the decomposition a reaction of this kind takes place :

$$2KClO_3 = KCl + KClO_4 + O_2.$$

The compound $KClO_4$, or *potassium perchlorate,* can be separated from the chloride by treating the mixture with cold water in which the chloride is easily soluble, while the perchlorate is practically insoluble. From the perchlorate, perchloric acid can be made in the same way that chloric acid is made from potassium chlorate, by treating with fluosilicic acid (see preparation of chloric acid). Perchloric acid is, however, much more stable in concentrated solution than the other oxygen compounds of chlorine, and if the perchlorate is treated with sulphuric acid, perchloric acid can be obtained from the mixture by distillation.

Pure perchloric acid, $HClO_4$, can be obtained in the form of a colorless fuming liquid. It is a dangerous substance to deal with, as it produces bad wounds when brought in contact with the flesh, and is very unstable and explosive. In contact with combustible substances in general it causes explosion in consequence of the ease with which it gives up oxygen and converts the combustible substances into gaseous products.

A hydrate of the formula $HClO_4 + H_2O$ or $H_3ClO_5$ is known. Further, there are some facts known that point to the existence of a second hydrate of the formula $HClO_4 + 2H_2O$.

**General.**—From the above it will be seen that the compounds of chlorine with hydrogen and oxygen form a series, the members of which bear a simple relation to one another. Beginning with hydrochloric acid the series is as follows:

| | |
|---|---|
| Hydrochloric acid, . . . . | $HCl$ |
| Hypochlorous acid, . . . . | $HClO$ |
| Chlorous acid, . . . . . . | $HClO_2$ |
| Chloric aid, . . . . . . . | $HClO_3$ |
| Perchloric acid, . . . . . | $HClO_4$ |

The successive members differ from each other by one atom of oxgen, the ratio between the hydrogen and the chlorine remaining the same throughout the series. While the compounds differ markedly from one another in many ways, they have some common features. Upon metals, and their oxides and hydroxides, all the members of the series act in general in the same way that hydrochloric acid does, the result being the formation of products which do not contain hydrogen, but do contain a metal in the place of the hydrogen. We have examples of these compounds in potassium chlorate, $KClO_3$, calcium hypochlorite, $Ca(ClO)_2$, potassium chlorite, $KClO_2$, and potassium perchlorate, $KClO_4$. All these compounds belong to the class called *salts*, which will presently be taken up. On the other hand, while there is a class of elements upon which hydrochloric acid does not act, the

oxygen compounds of the above series will in many cases act upon these elements and convert them into oxides. Thus sulphur and phosphorus, which are not acted on by hydrochloric acid, are converted into oxides by the oxygen compounds of chlorine.

Finally, the addition of oxygen to hydrogen and chlorine decreases the stability of the compound. Hydrochloric acid, for example, is characterized by great stability, while hypochlorous acid, HClO, as well as all the other members of the series, is characterized by instability. The larger the proportion of oxygen, however, the greater the stability of the compound. The most stable member of the series of oxygen compounds is perchloric acid. Another fact that is worthy of special notice is that the metal derivatives or salts of these acids are more stable than the acids themselves. Many of them can be heated to a comparatively high temperature without undergoing decomposition. This is most marked in the case of the perchlorates. It will be remembered that in decomposing potassium chlorate for the purpose of making oxygen the change takes place in two stages. In the first, potassium perchlorate is formed. In order to decompose this, however, the temperature must be raised considerably higher than that which was required to effect the breaking down of the chlorate.

**Compounds of Chlorine with Oxygen.**—The compounds of chlorine with oxygen are:

*Chlorine monoxide*, $Cl_2O$, and *chlorine dioxide*, $ClO_2$.

The first or *chlorine monoxide*, $Cl_2O$, is formed by the action of chlorine on dry mercury oxide:

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$

It is a gas which can easily be condensed to the liquid form. The specific gravity of its vapor gives the molecular weight corresponding to the formula $Cl_2O$. It is extremely unstable, breaking down under the influence of heat into chlorine and oxygen. With water it forms hypochlorous acid, thus:

$$Cl_2O + H_2O = 2HOCl.$$

A substance formed by treating a mixture of arsenic trioxide, $As_2O_3$, and potassium chlorate with nitric acid and by other methods has been described as a greenish-yellow gas which can be condensed to an extremely unstable liquid; and it is generally referred to under the name *chlorine trioxide*, the formula $Cl_2O_3$ being ascribed to it. The most careful investigation of this substance has, however, shown that it is not chlorine trioxide, but a mixture of chlorine dioxide with varying quantities of chlorine or free oxygen.

*Chlorine dioxide*, $ClO_2$, is a greenish-yellow gas of great instability. It can be condensed to a liquid which boils at $+9°$. It is always one of the products of the action of concentrated sulphuric acid upon potassium chlorate, and is formed in consequence of the decomposition of the chloric acid which is first set free:

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3;$$
$$6HClO_3 = 2HClO_4 + 2H_2O + 4ClO_2.$$

When moderately dilute hydrochloric acid acts upon potassium chlorate a greenish-yellow gas is formed which has been called *euchlorine*. It is a mixture of chlorine and chlorine dioxide, formed thus:

$$2KClO_3 + 4HCl = 2KCl + 2H_2O + 2ClO_2 + Cl_2.$$

Combustible substances burn in chlorine dioxide with violence. This action can be shown by putting a few small pieces of phosphorus under water in a glass vessel, and upon this a little potassium chlorate. If now a few drops of concentrated sulphuric acid are added through a long narrow tube or pipette, the phosphorus will be seen to burn under water. This is due to the liberation of chlorine dioxide, and the action of this compound upon the phosphorus.

When a solution of chlorine dioxide in water is treated with potassium hydroxide, potassium chlorite, $KClO_2$, is formed (see p. 118).

**Constitution of the Compounds of Chlorine with Hydrogen and Oxygen.**—To determine the constitution of unstable compounds which, when they break down at all, are almost completely disintegrated is difficult, and in many cases impossible. Our knowledge of the constitution of the oxygen acids of chlorine is for this reason extremely limited. Regarding the series of these compounds and comparing their composition with that of hydrochloric acid, it would appear that they are compounds of hydrochloric acid with different amounts of oxygen. But we have seen that chlorine and hydrogen are univalent elements, as is shown in hydrochloric acid, H–Cl. If each of the atoms in the molecule of hydrochloric acid is doing all it can in holding the other atom in combination, then, plainly, it is impossible for the molecule to take up oxygen directly and form a compound of the formula H–Cl–O or O–H–Cl. On the other hand, it is possible to conceive of the atoms chlorine, hydrogen, and oxygen as being united in such a way that hydrogen and chlorine shall be univalent and oxygen bivalent. This is represented in the formula Cl–O–H. Further, extensive study of compounds containing hydrogen and oxygen has made it appear extremely probable that in them the hydrogen is generally in combination with oxygen as represented in the above formula, and as is represented also in the formulas of such compounds as potassium hydroxide, K–O–H, calcium hydroxide, $Ca{<}{O-H \atop O-H}$, aluminium hydroxide,

$Al{\Big\langle}{O-H \atop O-H \atop O-H}$, etc. All the reasons for this cannot possibly be made clear without a knowledge of a great many facts which must be acquired gradually. As regards such hydroxides as those just referred to, the views expressed in the formulas given are certainly simpler than any others which have been proposed, and they are not contradicted by any known facts. Assuming then that in the acids of chlorine the hydrogen is in combination with oxygen, or that the compounds are hydroxides, we

have the formulas H–O–Cl, H–O–ClO, H–O–ClO$_2$, and H–O–ClO$_3$ for the four compounds. If, however, chlorine is univalent the additional oxygen cannot be in direct combination with the chlorine, and the only way in which the constitution of these compounds can be represented on the assumption that hydrogen and chlorine are univalent and oxygen bivalent is this: H–O–Cl, H–O–O–Cl, H–O–O–O–Cl, and H–O–O–O–O–Cl. These formulas have been used for some time, but strong opposition has been raised to them and they are now rapidly losing ground. They represent compounds in which oxygen atoms are in combination with oxygen atoms. But judging by the conduct of hydrogen dioxide and ozone, this kind of combination is a very unstable one. The acids of chlorine are unstable enough, but the one which contains the most oxygen is the most stable, and this we should hardly expect if the oxygen atoms are arranged as shown in the above formulas. This is not a fatal objection to these formulas, but it makes them, at least, appear improbable.

The view which now finds most support is based upon the conception that the valence of chlorine towards oxygen and towards oxygen and hydrogen, or towards hydroxyl as the group O–H is called, varies from univalence to septivalence ; that it is univalent in hydrochloric acid and in hypochlorous acid, trivalent in chlorous acid, quinquivalent in chloric acid, and septivalent in perchloric acid. This is shown in the formulas

$$H\text{–}O\text{–}Cl, \quad H\text{–}O\text{–}Cl{=}O, \quad H\text{–}O\text{–}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Cl}}}} \quad \text{and} \quad H\text{–}O\text{–}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Cl}}}}{=}O.$$

From a study of other similar compounds these compounds are regarded as derived from hydroxides, thus : Chlorous acid, O=Cl–O–H, is supposed to be formed from the hydroxide $Cl{\Big\langle}{\overset{\displaystyle OH}{\underset{\displaystyle OH}{OH}}}$ by loss of water ; chloric acid

from the hydroxide $Cl(OH)_5$ by loss of two molecules of water :

$$Cl(OH)_5 = ClO_2(OH) + 2H_2O ;$$

perchloric acid from the hydroxide $Cl(OH)_7$ by the loss of three molecules of water :

$$Cl(OH)_7 = ClO_3(OH) + 3H_2O.$$

When the acids are dissolved in water it is quite probable that in many cases the hydroxides are formed, but being unstable they cannot generally be isolated. The hydrate of perchloric acid, $HClO_4 + H_2O(H_3ClO_5)$, appears to be such a compound. It probably has the constitution represented by the formula $O_2Cl(OH)_3$. From the compound $Cl(OH)_7$ a series of compounds can be derived by successive losses of one molecule of water, as here shown :

$$Cl(OH)_7 \quad - H_2O = OCl(OH)_5 ;$$
$$OCl(OH)_5 \quad - H_2O = O_2Cl(OH)_3 ; \text{ and}$$
$$O_2Cl(OH)_3 \quad - H_2O = O_3Cl(OH).$$

The second and last products are the hydrate and the compound known as perchloric acid. While the evidence in favor of this view presented by these compounds themselves is very slight, the view is strongly supported by the conduct of certain analogous derivatives of the element iodine, which in many respects conducts itself like chlorine.

**Comparison of Chlorine and Oxygen.**—The power of chlorine to combine with other elements is nearly as great as that of oxygen. It combines with all other elements except fluorine, but does not form quite as great a variety of compounds as oxygen. Oxygen combines with several elements in three or four different proportions, but chlorine rarely combines in more than two proportions with one element. While in general chlorine and oxygen conduct themselves in the same way, there is a

very important difference between them, to which attention has already been called indirectly. There are some elements towards which oxygen has a stronger affinity than chlorine; and there are others towards which chlorine has a stronger affinity than oxygen. The former are the non-metals or acid-forming elements; the latter are the metals or base-forming elements. The difference is shown most readily by the fact that the chlorine compounds of the acid-forming elements are converted by water into oxygen compounds or hydroxides, while the oxides or hydroxides of the base-forming elements are converted into chlorides by the action of hydrochloric acid. This distinction is not a sharp one which can easily be made, for the conduct of an element is to a considerable extent dependent upon conditions, particularly of temperature, and a distinction which holds good under one set of conditions may possibly not hold good under another set. Still the above statements in regard to the conduct of the metals and non-metals towards chlorine and oxygen are in accordance with well-marked tendencies of the two classes of elements, as will appear more clearly.

Chlorine and oxygen being in general similar elements we should not expect them to combine readily with each other. Although they do combine indirectly in a number of proportions, none of the compounds are stable. There is a marked difference between these compounds and hydrochloric acid as regards the ease with which they are formed, and also as regards their stability. A marked difference between chlorine and oxygen is also to be found in their relations to hydrogen. While one volume of chlorine combines with one of hydrogen to form two volumes of hydrochloric acid gas, one volume of oxygen combines with two volumes of hydrogen, the three volumes of gas condensing to two volumes of water vapor. So also while, as we say, one atom of chlorine combines with one atom of hydrogen, one atom of oxygen combines with two atoms of hydrogen. What the difference between a bivalent and a univalent element consists in is

not known, but that the difference is something deep seated appears from the marked difference in conduct between chlorine and oxygen in combining with hydrogen.

# CHAPTER X.

**General.**—One cannot deal with chemical phenomena without constant reference to acids, and in the course of our study thus far a number of substances belonging to this class have been met with. It is now time to inquire what features these substances have in common which lead chemists to call them all acids. What is there in common between the heavy, oily liquid, sulphuric acid, the colorless gas, hydrochloric acid, and the unstable compounds chloric and hydrochlorous acids? To understand the common features requires some knowledge of a class of substances to which attention has already been given. These are substances like caustic potash and caustic soda, or potassium and sodium hydroxides which are called *alkalies,* which are the most marked representatives of the class of substances known as *bases.* These two classes, *acids* and *bases,* have the power to destroy the characteristic properties of each other. When an acid is brought in contact with a base in proper proportions, the characteristic properties of both the acid and the base are destroyed. They are said to *neutralize* each other. They form new products which are said to be neutral, which means that they have not the properties of an acid nor those of a base. This act of neutralization is an extremely important one, with which we have constantly to deal in chemical operations.

**A Study of the Act of Neutralization.**—The fact having been learned that acids and bases neutralize one another, the next thing to do is to study the act of neutralization as carefully as possible, and learn what chemical changes are involved in it. For this purpose we

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should select a number of acids and a number of bases and study their action upon one another. We may take sulphuric, hydrochloric, and nitric acids; and potassium, sodium, and calcium hydroxides. We know from many analyses that have been made that the composition of these substances is as follows:

$$
\begin{array}{ll}
\text{Hydrochloric acid,} \quad . \quad . \quad . \quad . \quad . & \text{HCl} \\
\text{Nitric acid,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . & \text{HNO}_3 \\
\text{Sulphuric acid,} \quad . \quad . \quad . \quad . \quad . & \text{H}_2\text{SO}_4 \\
\text{Potassium hydroxide,} \quad . \quad . \quad . \quad . & \text{KOH} \\
\text{Sodium hydroxide,} \quad . \quad . \quad . \quad . \quad . & \text{NaOH} \\
\text{Calcium hydroxide,} \quad . \quad . \quad . \quad . & \text{Ca(OH)}_2
\end{array}
$$

The first question to be answered is whether, in order to effect neutralization, definite quantities of the substances are necessary. To decide this, solutions of the acids and of the bases should be prepared and allowed to act upon one another in different proportions. But how shall we determine whether the solutions we are working with are acid, basic, or neutral? It has been found that all acids have the power to change the color of certain substances. For example, the dye litmus is blue. If a solution which is colored blue with litmus is treated with a drop or two of an acid, the color is changed to red. If now the red solution is treated with a few drops of a solution of a strong base, the blue color is restored. There are many other substances which change markedly in color by the addition of acids or bases. These facts furnish a means of recognizing whether a solution is acid or basic. Now, suppose that to a carefully measured quantity of one of the acid solutions a few drops of blue litmus is added. It will at once turn red. On adding slowly a solution of one of the bases the color will remain red as long as the solution is acid, but the instant it is basic it will turn blue. By noticing when the change in color takes place, it is possible to determine exactly how much of a certain basic solution is required to neutralize the quantity of the acid solution taken. If it is found in the case studied that

to neutralize 20 cc. of the acid solution 30 cc. of the basic solution are required, then, using the same solutions, it will be found in every experiment that the same quantities are required to effect neutralization, or that the change of color takes place whenever these proportions are reached. And no matter how the quantity of one of the liquids is varied, the quantity of the other required for neutralization varies in the same proportion. A great many experiments of this kind have been performed with many different acids, and what is true in one case has been found true in all. It appears, therefore, that *the act of neutralization is a definite one, which takes place between definite quantities of acid and base ; that for a certain quantity of base a certain quantity of acid is required to effect neutralization, and vice versa.*

The next question to be answered is, What is formed when the acid and base are neutralized? To determine this, larger quantities of acids should be neutralized with bases, and the substance or substances formed should then be studied. If hydrochloric acid is neutralized with sodium hydroxide a solid product, sodium chloride, is formed. The action takes place according to the following equation:

$$HCl + NaOH = NaCl + H_2O.$$

Hydrochloric acid and calcium hydroxide act thus:

$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O.$$

Nitric acid acts upon the three bases mentioned above as represented in these equations:

$$HNO_3 + KOH = KNO_3 + H_2O ;$$
$$HNO_3 + NaOH = NaNO_3 + H_2O ;$$
$$2HNO_3 + Ca(OH)_2 = Ca(NO_3)_2 + H_2O.$$

Sulphuric acid acts upon these same bases thus:

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O ;$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O ;$$
$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O.$$

The reactions which take place in these cases are typical of all reactions between acids and bases. One of the products formed is always water, the other is a compound which is without acid and basic properties, or which is neutral and differs from the acid in that it contains some other element in place of the hydrogen. This other element is the one which in the base is in combination with hydrogen and oxygen as a hydroxide. The simplest case is that of hydrochloric acid and either potassium or sodium hydroxide:

$$HCl + KOH = KCl + H_2O.$$

As has already been stated (see p. 111), we have here two forces operating to bring about the change: (1) the tendency of hydrogen to combine with hydroxyl (OH) to form water; and (2) the tendency of chlorine to unite with potassium. A similar statement may be made in regard to every reaction between an acid and a base.

**General Statements.**—Considering the facts treated of in the last paragraph, it appears:

(1) That an acid contains hydrogen;

(2) That a base contains a metal;

(3) That when an acid acts upon a base the hydrogen and metal exchange places;

(4) That the substance formed by substituting hydrogen for the metal of the base is water;

(5) That the substance obtained from the acid by substituting a metal for the hydrogen is neither an acid nor a base, but is generally neutral.

The last statement is subject to some modification, for reasons which in some cases are clear but in others are not apparent. It is true that in some cases after substituting a metal for the hydrogen the substance has an alkaline reaction, and in other cases an acid reaction.

**Definitions.**—We have already seen that hydrochloric acid and sulphuric acid act upon certain metals, as iron and zinc, and that the action consists in giving up hydrogen and taking up metal in its place. The products

of this action are the same in character as those formed by the action of acids on bases.

An *acid* is a substance containing hydrogen, which it easily exchanges for a metal, when treated with a metal itself, or with a compound of a metal, called a base.

A *base* is a substance containing a metal combined with hydrogen and oxygen. It easily exchanges its metal for hydrogen when treated with an acid.

The products of the action of an acid on a base are, first, *water*, and, second, a neutral substance called a *salt*.

In the examples above cited the products $KNO_3$, potassium nitrate ; $NaNO_3$, sodium nitrate ; $Ca(NO_3)_2$, calcium nitrate ; $K_2SO_4$, potassium sulphate ; $Na_2SO_4$, sodium sulphate ; $CaSO_4$, calcium sulphate, are salts. The relations between them and the acids from which they are derived will be easily recognized on comparing their formulas with those of the acids.

**Comparison of the Reaction between Acids and Hydroxides, and between Acids and Chlorides.**—The reaction between acids and hydroxides, or, as it is generally spoken of, between acids and bases, is quite similar in character to that which takes place between some acids and chlorides. This is illustrated by the reaction between sulphuric acid and sodium chloride, represented by the equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Here, as when the hydroxide is used, the acid is neutralized and the salt, sodium sulphate, $Na_2SO_4$, is formed. The other product, however, is hydrochloric acid instead of water. For the sake of closer comparison the two reactions may be written thus :

$$\left.\begin{array}{c} NaOH \\ NaOH \end{array} + \begin{array}{c} H \\ H \end{array}\right\} SO_4 = \left.\begin{array}{c} Na \\ Na \end{array}\right\} SO_4 + \begin{array}{c} HOH \\ HOH \end{array} ;$$

$$\left.\begin{array}{c} NaCl \\ NaCl \end{array} + \begin{array}{c} H \\ H \end{array}\right\} SO_4 = \left.\begin{array}{c} Na \\ Na \end{array}\right\} SO_4 + \begin{array}{c} HCl \\ HCl \end{array}.$$

The two reactions are thus seen to be of the same general character. That with the chloride does not take place

as readily as that with the hydroxide, and therefore is not as general. There are many acids which have not the power to decompose chlorides as sulphuric acid does; whereas, in general, any acid is neutralized by any metallic hydroxide. In some cases this reaction is an energetic one accompanied by a great evolution of heat; in others the reaction is not at all energetic. Both acids and bases differ very markedly from one another in some property which is spoken of in a vague sort of way as the strength. For the present it is sufficient to recognize that this difference is similar to the difference noticed between elements. Hydrogen and chlorine, for example, differ markedly in their power to act upon other substances, and chlorine is spoken of as the more energetic or active element.

**Other Similar Reactions.**—There are many other reactions like those which take place between acids and chlorides, and between acids and hydroxides. Another example is furnished by the sulphides and hydrosuphides, which are compounds that in some respects resemble oxides and hydroxides. The reactions which take place between the sulphur compounds and acids, and between the oxygen compounds and acids, are entirely analogous, as shown in the following equations:

$$K_2S \quad + 2HCl = 2KCl + H_2S;$$
$$K_2O \quad + 2HCl = 2KCl + H_2O;$$
$$CaS \quad + H_2SO_4 = CaSO_4 + H_2S;$$
$$CaO \quad + H_2SO_4 = CaSO_4 + H_2O;$$
$$KSH \quad + HCl = KCl + H_2S;$$
$$KOH \quad + HCl = KCl + H_2O;$$
$$Ca(SH)_2 + H_2SO_4 = CaSO_4 + 2H_2S;$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

The product formed in place of water is the corresponding compound of sulphur, $H_2S$. It will be observed that the hydrosulphides, or compounds which have the general composition $MSH$, neutralize the acids in the same sense that the hydroxides do. If hydroxides were not known, our conceptions of acids might easily be based upon the

relations of compounds to the hydrosulphides, and the substances now classed with the acids would be classed with them upon this basis. As we go on we shall see that there are other reactions of the same general character.

**Distinction between Acids and Bases.**—Although there is no difficulty in distinguishing between most acids and most bases, there are some compounds which act sometimes in one way and sometimes in the other. Sulphuric acid, nitric acid, and hydrochloric acid always act as acids, and sodium and potassium hydroxides always act as bases, but some substances which are generally basic will under some circumstances act as acids, and some which act as acids will occasionally act as bases. What is the standard? How shall we tell whether a substance is an acid or a base? We may take a pronounced acid, such as hydrochloric acid, and say that any hydroxide which has the power to neutralize this acid and form with it a salt shall be called a base ; and in the same way we may take a pronounced base, like potassium hydroxide, and say that any hydroxide which has the power to neutralize this shall be called an acid. Having made the division in this way, it would be found that a few substances would be included in both lists, or, in other words, some substances which are basic toward hydrochloric acid are acid toward potassium hydroxide. As an example, we may take aluminium hydroxide, $Al(OH)_3$. This neutralizes hydrochoric acid and forms aluminium chloride according to the equation

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O.$$

But it also neutralizes potassium hydroxide according to the equation

$$Al(OH)_3 + 3KOH = Al(OK)_3 + 3H_2O.$$

It may be said in regard to this case, as in regard to most other cases of the kind, that the hydroxide in question is basic toward nearly all substances toward which potassium hydroxide is basic ; whereas it is acid toward only three or four of the most energetic bases. Bearing

in mind, then, the fact that there are some exceptional cases, it may be said that the distinction between acids and bases is easily recognized.

**Metals or Base-forming Elements.**—The question, What is a metal? may fairly be asked. But unfortunately it is by no means an easy matter to give a satisfactory answer to the question. We can give examples of metals, such as iron, zinc, silver, calcium, magnesium, etc.; but when we attempt to find the distinguishing features of these substances we are somewhat at a loss to state them. In general, it may be said that to the chemist any element is a metal which with hydrogen and oxygen forms a base, or a product which has the power to neutralize acids. In general, any element which has the power to enter into an acid in the place of the hydrogen is called a metal, or is said to have metallic properties. This is the sense in which the word metal is used in this book. A better, though a longer, name for the metals is *base-forming elements*.

**Constitution of Acids and Bases.**—As has been pointed out, the bases are hydroxides, and these hydroxides are regarded as derived from water by the replacement of the hydrogen by metals. Examples of the hydroxides of univalent, bivalent, and trivalent metals were given in a previous chapter (see pp. 83–84). Similarly, the acids which contain oxygen are regarded as hydroxides, or as derived from water, as was stated when the subject of the constitution of the acids of chlorine was under consideration. This view is illustrated by the following formulas of some of the more common acids:

| | |
|---|---|
| Nitric acid, . . . . . . . | $(HO)NO_2$ |
| Sulphuric acid, . . . . . . | $(HO)_2SO_2$ |
| Phosphoric acid, . . . . . | $(HO)_3PO$ |
| Carbonic acid, . . . . . . | $(HO)_2CO$ |
| Metaphosphoric acid, . . . . | $(HO)PO_2$ |
| Nitrous acid, . . . . . . . | $(HO)NO$ |
| Arsenious acid, . . . . . . | $(HO)_3As$ |
| Hypochlorous acid, . . . . | $(HO)Cl$ |
| Perchloric acid, . . . . . . | $(HO)ClO_3$ |

There are three classes of acids represented in this list: (1) those with one, (2) those with two, and (3) those with three atoms of hydrogen in the molecule. Or, considering the compounds as hydroxides, these classes are: (1) those derived from one molecule, (2) those derived from two molecules, and (3) those derived from three molecules of water by replacement of half the hydrogen by something else. It is interesting to observe, also, that this something which replaces the hydrogen is in most cases an element in combination with oxygen or, if it is not in combination with oxygen, it has the power to take up more oxygen. Thus hypochlorous and arsenious acids are regarded as derived from water by the replacement of hydrogen in water by chlorine and arsenic as

$$\text{shown thus : } H\text{--}O\text{--}Cl \text{ and } \begin{matrix} H\text{--}O \\ H\text{--}O \\ H\text{--}O \end{matrix}\Big\rangle As. \quad \text{But, in each case,}$$

the element which is in combination with hydroxyl has the power to combine with oxygen. Hypochlorous acid forms the products $(HO)ClO$, $(HO)ClO_2$, and $(HO)ClO_3$, while arsenious acid forms arsenic acid $(HO)_3AsO$.

We may consider water as forming the connecting link between the oxygen acids and bases. If A stands for any acid-forming element, and B for any base-forming element, then the general formula of a base is $B(OH)$, and that of an oxygen acid $A(OH)$ or $O_xA(OH)$, in which $O_x$ stands for some number of oxygen atoms from one to three or four. We should then have these relations:

| | Bases. | Water. | Acids. |
|---|---|---|---|
| I. | $B'(OH)$ | HOH | $(O_xA)'(OH)$ |
| II. | $B''(OH)_2$ | HOH<br>HOH | $(O_xA)''(OH)_2$ |
| III. | $B'''(OH)_3$ | HOH<br>HOH<br>HOH | $(O_xA)'''(OH)_3$ |

In these general formulas $B''$ means any bivalent metal, and $B'''$ any trivalent metal; and $(O_xA)''$ means any

group of atoms which has the power to hold two hydroxyl groups in combination, and is therefore bivalent like $(O_2S)$, and $(O_xA)'''$ means a trivalent group like $(OAs)$.

**Constitution of Salts.**—The view held in regard to the constitution of salts is based directly upon those held in regard to the constitution of acids and bases. It is believed that when an oxygen acid acts upon a base the action takes place as represented in the following equation:

$$O_2N-O-\overline{|H + H-O|}-K = O_2N-O-K + H-O-H\,;$$

or in this:

$$O_2N-\overline{|O-H + H|}-O-K = O_2N-O-K + H-O-H.$$

In either case the salt formed appears as the acid, the hydrogen of which has been replaced by the metal. Whether the hydroxyl of the base unites with the hydrogen of the acid, or the hydroxyl of the acid unites with the hydrogen of the base, cannot be determined; and, as far as the constitution of the salt is concerned, it evidently makes no difference. The case stands thus: For reasons partly pointed out above, the bases are regarded as hydroxides; for similar reasons the acids are also regarded as hydroxides. Now, when an acid acts upon a base water and a product which differs from the acid in having the metal of the base in place of its hydrogen are formed. The simplest interpretation of this reaction is that given above. A case in which there appears to be no room for doubt as to what takes place is that of hydrochloric acid and a simple base like sodium hydroxide:

$$Cl-H + H-O-Na = ClNa + H-O-H.$$

It is highly probable that the reaction between acids and bases is always of this character.

**Basicity of Acids.**—In working with acids and bases it is noticed that some acids have the power to form but

one salt with a base like potassium hydroxide, while others have the power to form two or more salts with such a base. Thus, for example, hydrochloric acid, HCl, and nitric acid, $HNO_3$, can form but one salt with potassium hydroxide, and the reactions are represented in the following equations :

$$KOH + HCl = KCl + H_2O ;$$
$$KOH + HNO_3 = KNO_3 + H_2O.$$

If only half the quantity of base which is required to neutralize the acid is added, half the acid remains unchanged, and on evaporating the solution the excess of acid will pass off. So also, if only half the quantity of acid which is required to neutralize the base is added, half the base will remain unchanged. On the other hand, if an acid like sulphuric acid is taken, it is found that this has the power to form two distinct salts with potassium hydroxide, in one of which there is twice as much of the metal as in the other. The reactions are represented thus :

$$KOH + H_2SO_4 = KHSO_4 + H_2O ;$$
$$2KOH + H_2SO_4 = K_2SO_4 + H_2O.$$

If to a given quantity of sulphuric acid only half the quantity of potassium hydroxide which is required to neutralize it is added, the first reaction takes place ; but if the act of neutralization is complete the second reaction takes place. An acid of this kind can, further, form one salt with two bases, in which one of the hydrogen atoms of the acid is replaced by one metal and the other by a second metal.

The different properties of the two kinds of acids referred to are ascribed to differences in constitution. In the molecule of hydrochloric acid, as in that of nitric acid, there is but one atom of hydrogen according to the views at present held. If, therefore, the act of neutralization takes place in each molecule it is complete, and the salt is said to be a *neutral* or *normal salt.* In sulphuric acid, however, there are two atoms of hydrogen

in each molecule, and either one or both of these may be replaced. If only one is replaced, a salt of the general formula $MHSO_4$ is obtained. This is still an acid, while also partly a salt. It is in fact an *acid salt* or a *salt acid.*

Acids like hydrochloric and nitric acids have not the power to form acid salts. They are called *monobasic acids.* While acids like sulphuric acid, which can form two salts with one base, one of which is acid, are called *dibasic acids.*

Monobasic acids are those which contain but one replaceable hydrogen atom in the molecule. Dibasic acids are those which contain two replaceable hydrogen atoms in the molecule.

Similarly, there are *tribasic acids*, like phosphoric acid, $H_3PO_4$, arsenic acid, $H_3AsO_4$, etc.; *tetrabasic acids*, like pyrophosphoric acid, $H_4P_2O_7$; *pentabasic acids*, like periodic acid, $H_5IO_6$; etc., etc. The higher the basicity of the acid the greater the variety of salts it can yield.

**Acidity of Bases.**—Just as we speak of monobasic, dibasic, tribasic acids, etc., so we distinguish between bases of different acidity. Thus there are the *monacid bases*, like potassium and sodium hydroxides, $KOH$ and $NaOH$; *diacid bases*, like calcium and barium hydroxides, $Ca(OH)_2$ and $Ba(OH)_2$; *triacid bases*, like aluminium and ferric hydroxides, $Al(OH)_3$ and $Fe(OH)_3$; etc., etc.

If a monobasic acid acts upon a monacid base, one molecule of one forms a salt with one molecule of the other, and, in general, no other reaction between the two is possible. If a monobasic acid acts upon a diacid base two reactions are possible, just as when a monacid base acts upon a dibasic acid. Thus, when, for example, hydrochloric acid acts upon zinc hydroxide, $Zn(OH)_2$, two reactions are possible:

$$Zn(OH)_2 + HCl = Zn{<}^{Cl}_{OH} + H_2O;$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O.$$

The compound $ZnCl(OH)$ is still basic, just as the salt $KHSO_4$ is still acid, and it is called a *basic salt.* Simi-

larly, a triacid base can form three salts with a monobasic acid as, for example, in the case of bismuth hydroxide and nitric acid, in which three reactions are possible :

$$\mathrm{Bi} \begin{cases} \mathrm{OH} \\ \mathrm{OH} \\ \mathrm{OH} \end{cases} + \mathrm{HNO_3} = \mathrm{Bi} \begin{cases} \mathrm{NO_3} \\ \mathrm{OH} \\ \mathrm{OH} \end{cases} + \mathrm{H_2O};$$

$$\mathrm{Bi} \begin{cases} \mathrm{OH} \\ \mathrm{OH} \\ \mathrm{OH} \end{cases} + 2\mathrm{HNO_3} = \mathrm{Bi} \begin{cases} \mathrm{NO_3} \\ \mathrm{NO_3} \\ \mathrm{OH} \end{cases} + 2\mathrm{H_2O};$$

$$\mathrm{Bi} \begin{cases} \mathrm{OH} \\ \mathrm{OH} \\ \mathrm{OH} \end{cases} + 3\mathrm{HNO_3} = \mathrm{Bi} \begin{cases} \mathrm{NO_3} \\ \mathrm{NO_3} \\ \mathrm{NO_3} \end{cases} + 3\mathrm{H_2O}.$$

The salts $\mathrm{Bi} \begin{cases} \mathrm{NO_3} \\ \mathrm{(OH)_2} \end{cases}$ and $\mathrm{Bi} \begin{cases} \mathrm{(NO_3)_2} \\ \mathrm{OH} \end{cases}$ are basic salts or basic nitrates of bismuth, while the salt $\mathrm{Bi(NO_3)_3}$ is the neutral or normal salt.

**Salts.**—From the above it appears that there are three classes of salts : (1) *Normal salts*, which are derived from the acids by replacement of all the acid hydrogen atoms by metal atoms ; (2) *Acid salts*, which are derived from the acids by replacement of part of the hydrogen by metal atoms ; and (3) *Basic salts*, which are derived from the bases by neutralization of part of the basic hydroxyl by acids. Normal salts are generally neutral ; or, if by a neutral substance is meant one which has not the power to form salts with acids nor with bases, then the expression normal salt is synonymous with neutral salt. But, strange to say, some normal salts have what is called an acid reaction, and others have an alkaline or basic reaction. Thus a normal salt of a weak acid with a strong base as sodium carbonate, $\mathrm{Na_2CO_3}$, has an alkaline reaction. So also a normal salt of a strong acid with a weak base may have an acid reaction, as in the case of copper sulphate, $\mathrm{CuSO_4}$. As generally used, the expression neutral salt means a salt which exhibits neither an acid nor an alkaline reaction.

In naming acid salts various methods are adopted. In the case of a dibasic acid, the only distinction necessary is between the acid and the normal salts. The expres-

sions *acid potassium sulphate* and *normal potassium sulphate* mean, of course, the salts which have the formulas $KHSO_4$ and $K_2SO_4$, and there is no danger of confusion. We may, however, use the names *mono-potassium sulphate* and *di-potassium sulphate*, or *primary* and *secondary potassium sulphates*. The last names are convenient and readily convey to the mind the nature of the salt spoken of. Just as dibasic acids yield primary and secondary salts, so tribasic acids yield primary, secondary, and tertiary salts. For example, phosphoric acid yields three classes of salts: *primary phosphates*, of the general formula $MH_2PO_4$; *secondary phosphates*, of the general formula $M_2HPO_4$; and *tertiary phosphates*, of the general formula $M_3PO_4$. The phosphates of the first two classes are called, in general, *acid phosphates*. The tertiary phosphate is identical with the normal phosphate. In naming basic salts there is no difficulty in the simplest cases. Thus, taking the three bismuth nitrates the formulas of which are given above, the one of the formula $Bi \begin{cases} NO_3 \\ (OH)_2 \end{cases}$ is called the *mono-nitrate;* that of the formula $Bi \begin{cases} (NO_3)_2 \\ OH \end{cases}$, the *di-nitrate;* and that of the formula $Bi(NO_3)_3$, the tri-nitrate or *normal nitrate.*

There are many cases which are much more complicated than any of those referred to above. Thus, there are basic salts formed by dibasic acids and diacid bases, by dibasic acids and triacid bases, etc. There is, for example, a basic copper carbonate formed by the partial neutralization of two molecules of copper hydroxide, $Cu(OH)_2$, by one molecule of carbonic acid, $CO(OH)_2$. The relations will be seen by the aid of the following equation, in which the structural formulas of copper hydroxide and of carbonic acid are used:

$$\begin{matrix} Cu{<}^{OH}_{OH} \\ Cu{<}^{OH}_{OH} \end{matrix} + {}^{HO}_{HO}{>}CO = \begin{matrix} Cu{<}^{OH}_{O} \\ Cu{<}^{O}_{OH} \end{matrix}{>}CO + 2H_2O.$$

The salt is basic.

**Acid Properties and Oxygen.**—Almost all those sub-
stances which are called acids contain oxygen, as, for
example, nitric acid, $HNO_3$; sulphuric acid, $H_2SO_4$; phos-
phoric acid, $H_3PO_4$; silicic acid, $H_2SiO_3$; carbonic acid,
$H_2CO_3$; boric acid, $H_3BO_3$; etc. The presence of oxygen
in acids was recognized by Lavoisier. As he showed
its presence in acids to be general, and as he found
that several elements and some compounds are con-
verted into acids by combination with oxygen, he con-
cluded that this element is an essential constituent of all
acids, and therefore called it oxygen, a name which, as
already stated (see p. 28), means the acid-former. Ac-
cording to Lavoisier, hydrochloric acid, like other acids,
contained oxygen, and this view prevailed for many years.
As has been pointed out under the head of Chlorine,
many investigations were undertaken with the object of
determining whether this element does or does not con-
tain oxygen, the result being to show that in chlorine,
and consequently in hydrochloric acid, there is no oxygen.
Several acids are now known which are like hydrochloric
acid in this respect, but the latter is the best known ex-
ample. Similar compounds are hydrobromic acid, $HBr$;
hydriodic acid, $HI$; and hydrocyanic acid, $HCN$. The
number of these acids is, however, quite small, and it is
undoubtedly true that, of the compounds which we com-
monly call acids, by far the larger number contain
oxygen as an essential constituent. Further, some com-
pounds which are basic can be converted into acids by
introducing oxygen into them.

On the other hand, there are many compounds which
do not contain oxygen which exhibit reactions entirely
analogous to those of the acids. There are for example
compounds containing sulphur which combine with sul-
phides, and others containing chlorine which combine
with chlorides in much the same way that the oxygen
acids combine with oxides, and the compounds formed
are analogous to ordinary salts, only they contain
sulphur or chlorine in place of oxygen. Thus, there is
a compound of arsenic and sulphur of the composition
$H_3AsS_4$, known as sulpharsenic acid, which is analo-

gous to the oxygen compound arsenic acid, $H_3AsO_4$.  When arsenic acid is treated with potassium hydroxide, KOH, this reaction takes place :

$$H_3AsO_4 + 3KOH = K_3AsO_4 + 3H_2O.$$

So, too, when sulpharsenic acid is treated with potassium hydrosulphide this reaction takes place :

$$H_3AsS_4 + 3KSH = K_3AsS_4 + 3H_2S.$$

As many such sulphur compounds are decomposed by water yielding the corresponding oxygen compounds, and as most such reactions must be studied in solution in water, a good reason for the fact that they are not as numerous as the oxygen acids will be seen.

Just as sulphur acids act upon sulphur bases to form sulphur salts, so there are what may be called chlorine acids which act upon chlorine bases to form chlorine salts.  For example, there is a compound, $H_2PtCl_6$, known as chlorplatinic acid, which with chlorides forms well-marked salts :

$$H_2PtCl_6 + 2KCl = K_2PtCl_6 + 2HCl.$$

The product formed in the reaction represented by this equation is known as potassium chlorplatinate.  The reaction is analogous to the following, in which oxygen compounds take part :

$$H_2PtO_3 + 2KOH = K_2PtO_3 + H_2O.$$

In the chlorine compounds two atoms of the univalent element chlorine take the place of each atom of the bivalent oxygen.  Many such compounds are known ; but in working with them the same difficulty arises that was referred to above in speaking of the sulphur compounds ; many of the chlorides which are capable of forming chlorine salts are decomposed by water and converted into oxygen acids.  Therefore, if we start with a chlorine acid and work in water solution the probability is that

the product obtained will be an oxygen compound. The fact that the oxygen acids are the most prominent is partly to be ascribed to the fact that water is in such general use as a solvent. The analogous solvent for the sulphur compounds would be liquid hydrogen sulphide, $H_2S$, but at ordinary temperatures this is a gas, and it is, therefore, impossible to work with the sulphur compounds under conditions analogous to those under which we work with the oxygen compounds. The same statement applies to the chlorine compounds for which the analogous solvent would be liquid hydrochloric acid, HCl,—not the solution of the gas in water.

**Nomenclature of Acids.**—The names of the acids of chlorine illustrate some of the principles of nomenclature in use in chemistry. The acid of the series which is best known is called chloric acid. In naming acids the suffix *ic* is always used in naming the principal member of a group of acids containing the same elements. This is seen in the names hydrochloric, sulphuric, nitric, phosphoric, silicic, carbonic, acetic, etc. If there are two acids containing the same elements, that one of the two which contains the smaller proportion of oxygen is given a name ending in *ous*. Thus we have the two series:

| | | | | |
|---|---|---|---|---|
| Chloric acid, | $HClO_3$ | Chlorous acid, | $HClO_2$ |
| Sulphuric acid, | $H_2SO_4$ | Sulphurous acid, | $H_2SO_3$ |
| Nitric acid, | $HNO_3$ | Nitrous acid, | $HNO_2$ |
| Phosphoric acid, | $H_3PO_4$ | Phosphorous acid, | $H_3PO_3$ |

For most cases which present themselves this method of naming will suffice, but in others the number of acids known is larger than two, as, for example, in the series of chlorine acids. In such cases recourse is had to prefixes. If there is an acid known containing a smaller proportion of oxygen than the one whose name ends in *ous*, it is generally designated by means of the prefix *hypo*, which is derived from the Greek ὑπό, signifying under. Thus there are the following examples: Hypochlorous acid, HClO; hyposulphurous acid, $H_2SO_2$; hyponitrous acid, $H_2N_2O_2$; and hypophosphorous acid,

$H_3PO_2$. It will be seen on comparing the formulas of these acids with those above given that they differ from them in a very simple way.

In the series of chlorine acids there is one which contains a larger proportion of oxygen than chloric acid. It is called perchloric acid, the Latin prefix *per* signifying here very or fully. Similarly there is a perbromic acid and a permanganic acid. Other cases arise, but they are of a more or less special character, and the compounds are given special names according to circumstances.

**Nomenclature of Bases.**—As pointed out above, a base is a compound of a metal with hydrogen and oxygen. The bases are commonly known as hydroxides; and in order to distinguish between the hydroxides of the different metals, the names of the metals are put before the name hydroxide, as in naming the oxides and chlorides. Thus, as has been seen, caustic soda, $NaOH$, is called sodium hydroxide, etc. It is necessary in some cases to distinguish between two hydroxides of the same metal. This is done by using the suffixes *ous* and *ic* in the same sense as they are used in naming oxides and chlorides. Thus ferric hydroxide has the composition $Fe(OH)_3$, and ferrous hydroxide the composition $Fe(OH)_2$; cuprous hydroxide is $Cu(OH)$, and cupric hydroxide $Cu(OH)_2$, etc. These compounds are sometimes called *hydrates*, and there are some good reasons for using this name, as will be more fully shown in a later paragraph. On the other hand, compounds in which water as such is regarded as present are called hydrates, and there is danger of confusion if the same name is used to designate what are believed to be two entirely different classes of compounds. As examples of hydrates we have salts with their water of crystallization, chlorine hydrate, $Cl_2 + 8H_2O$; hydrochloric acid hydrate, $HCl + 2H_2O$; etc. While some of the compounds which are commonly regarded as hydrates should probably be classed with the hydroxides, there seem to be two classes, and it is therefore desirable to have two names.

**Nomenclature of Salts.**—Theoretically every metal can yield a salt with every acid. The salts derived from a

given acid receive a general name, and this general
name is qualified in each case by the name of the metal
contained in the salt. Thus, all the salts derived from
nitric acid are called *nitrates;* all the salts derived from
chloric acid are called *chlorates;* the salts of sulphuric
acid are called *sulphates;* * the salts of phosphoric acid
are called *phosphates;* * etc. So too, further, the salts of
chlorous acid are called *chlorites;* those of nitrous acid,
*nitrites;* those of sulphurous acid, *sulphites;* etc., etc.
It will be noticed that the final syllable of the name
of the salt differs according to the name of the acid. If
the name of the acid ends in *ic*, the name of the salt de-
rived from it ends in *ate*. If the name of the acid ends
in *ous*, the name of the salt ends in *ite*. To dis-
tinguish between the different salts of the same acid,
the name of the metal contained in it is prefixed.
Thus, the potassium salt of nitric acid is called po-
tassium nitrate, the sodium salt is called sodium ni-
trate; the calcium salt of sulphuric acid is called calcium
sulphate; the magnesium salt of nitrous acid is magne-
sium nitrite; the calcium salt of hypochlorous acid is
calcium hypochlorite; etc., etc. If a metal forms two
salts with the same acid in one of which the valence of
the metal is lower than in the other, the one in which
the valence of the metal is lower is designated by
means of the suffix *ous*, while the one in which the
valence of the metal is higher is designated by means of
the suffix *ic*. Thus there are two series of salts of iron
which correspond to the two chlorides $FeCl_2$ and $FeCl_3$.
In one series the iron appears to be bivalent, in the
other trivalent. Examples are, $Fe(NO_3)_2$ and $Fe(NO_3)_3$;
$FeSO_4$ and $Fe_2(SO_4)_3$; etc. Those salts in which the
iron is bivalent are called ferrous salts, as ferrous
nitrate, ferrous sulphate, etc.; and those in which it is
trivalent are called ferric salts, as ferric nitrate, ferric
sulphate, etc. Similarly there are two series of copper

* Strictly speaking, the salts of sulphuric acid should be called *sul-
phurates*, and those of phosphoric acid *phosphorates*, but for the sake of
euphony and convenience these names are shortened to the above forms.

salts known as cuprous and cupric salts; and two series of mercury salts known as mercurous and mercuric salts.

If the salts of hydrochloric acid were named in accordance with the principle just explained, they would be called *hydrochlorates*, and this name is sometimes used for complex salts, but in the case of the salts of the metals it will be observed that these are identical with the products formed by direct combination of the metals with chlorine. Thus, hydrochloric acid and zinc act as represented in the equation

$$Zn + 2HCl = ZnCl_2 + H_2;$$

while zinc and chlorine act thus:

$$Zn + Cl_2 = ZnCl_2.$$

In each case the same product, $ZnCl_2$, is formed. But these compounds of metals with chlorine are called *chlorides*, as has already been explained. Hence for these cases the name *hydrochlorate* is unnecessary.

The name hydrate to which reference was made in a paragraph above suggests a salt of hydric acid. Potassium hydrate signifies the potassium salt of this acid or of water. In one sense this is a proper name for the compound. It is water in which a part of the hydrogen is replaced by a metal, and it is in this respect like a salt. While, however, there is an unmistakable analogy between the formation of a metallic hydroxide from water and that of a salt from an acid, it appears, on the whole, wise not to class water with the acids nor with the bases, but rather to regard it as the connecting link between the two classes. We shall see later that the similar compounds hydrogen sulphide, $H_2S$, and hydrogen selenide, $H_2Se$, have much more marked acid properties than water. When treated with metallic hydroxides they form salts of the general formulas $M_2S$ and $M_2Se$.

# CHAPTER XI.

## NATURAL CLASSIFICATION OF THE ELEMENTS—THE PERIODIC LAW.

**Historical.**—It has long been known that simple relations exist between the atomic weights of some elements which resemble one another closely. Thus chlorine, bromine, and iodine are very similar elements. Their atomic weights are 35.18, 79.34, and 125.89 respectively. It will be seen that the atomic weight of bromine, 79.34, is approximately the mean of those of chlorine and iodine. We have

$$\frac{35.18 + 125.89}{2} = 80.53.$$

A similar group is that of sulphur, selenium, and tellurium, which resemble one another as closely as chlorine, bromine, and iodine do. The atomic weights are $S = 31.83$, $Se = 78.42$, and $Te = 126.52$. We have here

$$\frac{31.83 + 126.52}{2} = 79.17.$$

Other groups are those of phosphorus, 30.79, vanadium, 50.99, and arsenic, 74.44:

$$\frac{30.79 + 74.44}{2} = 52.61;$$

lithium, 6.97, sodium, 22.82, and potassium, 38.82:

$$\frac{6.97 + 38.82}{2} = 22.89.$$

In 1863–64 J. A. R. Newlands called attention to the fact that if all the elements are arranged in a table in the order of their atomic weights, beginning with that one which has the lowest atomic weight and ending with that one which has the highest atomic weight, provided they are arranged horizontally in groups of seven, placing the eighth under the first, the ninth under the second, etc., then similar elements would fall in the same perpendicular line. Newlands' arrangement was quite imperfect, and it required considerable modification in order to make it appear at all satisfactory. In 1869 and 1870 two papers appeared, one by D. Mendeléeff and the other by Lothar Meyer, in which these relations are treated in a masterly manner, and it was then seen that one of the most important laws of chemistry had been discovered. Everything learned since then has only made it appear more and more certain that the law which is known as the *periodic law* is a fundamental law of chemistry.

**Arrangement of the Elements.**—Mendeléeff and Lothar Meyer have proposed several arrangements for the purpose of making clear the connection between the properties and atomic weights of the elements. Those which have proved most useful will first be given, and then the connection between the atomic weights and properties will be discussed briefly. The different arrangements are to be regarded only as different ways of expressing the same law, and no one of them is perfect. The investigation of the relations between the atomic weights and the properties of the elements has not yet been pushed far enough to justify a final opinion as to the character of the relations, but it has nevertheless reached a stage in which we are justified in stating that these relations are general and deep-seated.

**MENDELÉEFF'S TABLE I.**

| SERIES. | GROUP I. — R₂O. | GROUP II. — RO. | GROUP III. — R₂O₃. | GROUP IV. RH₄, RO₂. | GROUP V. RH₃, R₂O₅. | GROUP VI. RH₂, RO₃. | GROUP VII. RH, R₂O₇. | GROUP VIII. — RO₄. |
|---|---|---|---|---|---|---|---|---|
| 1 | H = 1 | | | | | | | |
| 2 | Li = 7 | Be = 9.1 | B = 11 | C = 12 | N = 14 | O = 16 | F = 19 | |
| 3 | Na = 23 | Mg = 24.4 | Al = 27 | Si = 28 | P = 31 | S = 32 | Cl = 35.5 | |
| 4 | K = 39.1 | Ca = 40 | Sc = 44 | Ti = 48.1 | V = 51.2 | Cr = 52.3 | Mn = 55 | Fe = 56, Ni = 58.5, Co = 59.1, Cu = 63.3 |
| 5 | (Cu) = 63.3 | Zn = 65.4 | Ga = 69.9 | Ge = 72 | As = 75 | Se = 79 | Br = 80 | |
| 6 | Rb = 85.4 | Sr = 87.5 | Y = 89 | Zr = 90.7 | Nb = 94.2 | Mo = 95.9 | — = 100 | Rh = 103, Ru = 103.8, Pd = 106, Ag = 107.9 |
| 7 | (Ag) = 107.9 | Cd = 112 | In = 113.7 | Sn = 118 | Sb = 120.3 | Te = 125.2 | I = 126.9 | |
| 8 | Cs = 132.9 | Ba = 137 | La = 138.5 | Ce = 141.5 | Di = 145 | — | — | — |
| 9 | (—) | — | — | — | — | — | — | Ir = 193.1, Pt = 194.8, Os = 200, Au = 196.7 |
| 10 | — | — | Yb = 173.2 | — | Ta = 182.8 | W = 184 | — | |
| 11 | (Au) = 196.7 | Hg = 200.4 | Tl = 204.1 | Pb = 206.9 | Bi = 208 | — | — | — |
| 12 | — | — | — | Th = 233.4 | — | U = 239 | — | — |

MENDELÉEFF'S TABLE II.

|  |  |  | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|---|---|
| $R_2O$ | I. |  | Li = 7 | K 39 | Rb 85 | Cs 133 | — — | — — |
| RO | II. |  | Be = 9 | Ca 40 | Sr 87 | Ba 137 | — — | — — |
| $R_2O_3$ | III. |  | B = 11 | Sc 44 | Y 89 | La 138 | Yb 173 | — — |
| $RO_2$ | IV. | $(H_4C)$ | C = 12 | Ti 48 | Zr 90 | Ce 142 | — — | Th 231 |
| $R_2O_5$ | V. | $(H_3N)$ | N = 14 | V 51 | Cb 94 | Di 146 | Ta 182 | — — |
| $RO_3$ | VI. | $(H_2O)$ | O = 16 | Cr 52 | Mo 96 | — — | W 184 | U 240 |
| $R_2O_7$ | VII. | (HF) | F = 19 | Mn 55 | — — | — — | — — | — — |
| $RO_4$ |  |  |  | Fe 56 | Ru 103 | — — | Os 192? | — — |
|  | VIII. |  |  | Co 58 | Rh 104 | — — | Ir 193 | — — |
|  |  |  |  | Ni 59 | Pd 106 | — — | Pt 195 | — — |
| $R_2O$ | I. | H = 1 | Na=23 | Cu 63 | Ag 108 | — — | Au 196 | — — |
| RO | II. |  | Mg 24 | Zn 65 | Cd 112 | — — | Hg 200 | — — |
| $R_2O_3$ | III. |  | Al 27 | Ga 69 | In 113 | — — | Tl 204 | — — |
| $RO_2$ | IV. | $(H_4R)$ | Si 28 | Ge 72 | Sn 118 | — — | Pb 206 | — — |
| $R_2O_5$ | V. | $(H_3R)$ | P 31 | As 75 | Sb 120 | — — | Bi 209 | — — |
| $RO_3$ | VI. | $(H_2R)$ | S 32 | Se 79 | Te 125? | — — | — — | — — |
| $R_2O_7$ | VII. | (HR) | Cl 35.5 | Br 80 | I 127 | — — | — — | — — |

In the above tables the approximate atomic weights are used instead of those which have been determined and calculated with the greatest care. For most purposes in the laboratory the approximate figures answer well enough, and they are most commonly used. In the following table of Lothar Meyer the refined atomic weights (as calculated by Meyer and Seubert) are used. The difference between the two sets of figures is in most cases very slight. The atomic weights adopted in this book are those calculated by F. W. Clarke (see "The Constants of Nature," Part V, 1897).

NATURAL SYSTEM OF THE ELEMENTS. (LOTHAR MEYER.)

Hydrogen, H = 1.

| A I. B | A II. B | A III. B | A IV. B | A V. B | A VI. B | A VII. B | VIII. |
|---|---|---|---|---|---|---|---|
| Li, 7.01 | Be, 9.08 | B, 10.9 | C, 11.97 | N, 14.01 | O, 15.96 | F, 19.06 | |
| Na, 23 | Mg, 23.94 | Al, 27.04 | Si, 28 | P, 30.96 | S, 31.98 | Cl, 35.37 | |
| K, 39.03 | Ca, 39.91 | Sc, 43.97 | Ti, 48 | V, 51.1 | Cr, 52.45 | Mn, 54.8 | Fe, 55.88, Co, 58.74, Ni, 58.56 |
| Cu, 63.18 | Zn, 64.88 | Ga, 69.9 | Ge, 72.32 | As, 74.9 | Se, 78.87 | Br, 79.76 | |
| Rb, 85.2 | Sr, 87.3 | Y, 88.9 | Zr, 90.4 | Cb, 93.7 | Mo, 95.9 | | Ru, 103.5, Rh, 104.1, Pd, 106.2 |
| Ag, 107.66 | Cd, 111.7 | In, 113.4 | Sn, 117.4 | Sb, 119.6 | Te, 125 | I, 126.54 | |
| Cs, 132.7 | Ba, 136.9 | La, 138 | Ce, 141.2 | Di, 142.1 | | | |
| | E, 166 | Yb, 172.6 | | Ta, 182 | W, 183.6 | | Os, 191, Ir, 192.5, Pt, 194.3 |
| Au, 196.7 | Hg, 199.8 | Tl, 203.7 | Pb, 206.4 | Bi, 207.3 | | | |
| | | | Th, 232 | | U, 239.8 | | |
| 1 [2, 3] | 2 [1] | 3 [1] | 4 [2] | 5 [3] | 6 [2] | 7 [1] | 8 [2, 3, 4] |

In Mendeléeff's Table I the elements are arranged in horizontal lines, beginning with lithium. When the eighth element in the order of the increasing atomic weights is reached it is found that it is very much like lithium. It is sodium. If this is placed below lithium, and the next six elements in the same horizontal line, when the fifteenth element is reached, it is found like the eighth to be similar to lithium. Up to and including manganese there are twenty-one elements excluding hydrogen. These fall then naturally into three series of seven members each, and placing these horizontally, those elements which fall in the same perpendicular lines have the same general character. This is seen most strikingly in Group I, in which lithium, sodium, and potassium fall, and in Group V, in which nitrogen, phosphorus, and vanadium fall; but there is no difficulty in recognizing the similarity in the other groups. The three elements following manganese, viz., iron, nickel, and cobalt, are very much alike, and they certainly do not belong in Groups I, II, and III, while the next element, copper, has some properties which ally it to the members of Group I. The next six elements fall in Groups II to VII, and are evidently in place, and the six following fall in Groups I to VI, and are also in their proper places, as far as their properties are concerned. After molybdenum in the sixth series comes a blank which means that there is no element to fill that place, but that probably 'there is one undiscovered which has the atomic weight approximately 100, and has properties which are similar to those of manganese. Then follow three elements which resemble one another as closely as iron, nickel, and cobalt do. These do not belong in Groups I, II, and III, but form a small independent group. These two groups of three elements occur at the end of the fourth and sixth series respectively. We should therefore expect to find a similar group at the end of the eighth series. No such group is known, however, though at the end of the tenth series, where we should look for the next similar small group, there are the three elements iridium, platinum, and osmium. The elements

of series 2 beginning with lithium and ending with fluorine differ in some respects quite markedly from all the other elements, as will be seen when they are taken up. Beginning with sodium, it will be seen that there are two series of seven elements and a short series of three; then again two series of seven and a series of three; and, although the following series are imperfect, it is not difficult to recognize that the same general arrangement of the elements holds good to the end. A series of seven elements is called a *short period;* while two short periods with the accompanying three similar elements constitute what is called a *long period.*

In Mendeléeff's Table II the long periods are arranged in perpendicular lines, each long period beginning and ending with a short period and having a side group of three elements in the middle. Thus in the column beginning with potassium there is, first, the short period potassium to manganese, then the side group iron, cobalt, nickel, and then the short period copper to bromine. In this table similar elements occur in the same horizontal lines. Thus in one line there are lithium, potassium, rubidium, and cæsium; in another sulphur, selenium, and tellurium; and in another chlorine, bromine, and iodine.

The symbols at the top of each column in Table I have reference to the general formulas of the compounds which the elements in each group form with oxygen and with hydrogen. Beginning with Group I, the general formula of the oxygen compounds of the members of this group is $R_2O$, in which R represents any element of that group; the general formula of the oxygen compounds of the members of Group II is $RO$; and so on. It will be observed that the oxygen compounds grow more and more complex from Group I to Group VII. Writing $RO$, $RO_2$, and $RO_3$ with doubled formulas, thus: $R_2O_2$, $R_2O_4$, and $R_2O_6$, the series of oxygen compounds is represented as below:

$$R_2O, \quad R_2O_2, \quad R_2O_3, \quad R_2O_4, \quad R_2O_5, \quad R_2O_6, \quad R_2O_7.$$

As regards the general formula of the oxygen compounds of the members of Group VIII, it must be said that it does not in general correspond to the composition $RO_4$. Osmium and ruthenium do, however, form the oxides $OsO_4$ and $RuO_4$.

There is also regularity in the composition of the hydrogen compounds. Beginning with Group VII, those members which combine with hydrogen form compounds of the general formula $RH$, as, for example, $ClH$, hydrochloric acid ; $FH$, hydrofluoric acid ; etc. Those members of Group VI which combine with hydrogen form compounds of the general formula $RH_2$, as, for example, water, $H_2O$, and hydrogen sulphide, $H_2S$. The maximum power of combining with hydrogen is met with in Group IV, in which occur the elements carbon and silicon. These form the hydrogen compounds $CH_4$ and $SiH_4$. The members of Groups I, II, and III do not readily form compounds with hydrogen. A few are known, but they are quite unstable.

The hydroxides vary in composition from the simple form $R(OH)$ to $R(OH)_7$. While in the first four groups well-marked examples of the hydroxides $R(OH)$, $R(OH)_2$, $R(OH)_3$, and $R(OH)_4$ are found, in the fifth group the hydroxides have not the general formula $R(OH)_5$, though several of them have the formula $OR(OH)_3$, as phosphoric, arsenic, and antimonic acids, which are respectively $OP(OH)_3$, $OAs(OH)_3$, and $OSb(OH)_3$. These may be regarded as derived from the hydroxides of the general formula $R(OH)_5$ by loss of water :

$$R(OH)_5 = OR(OH)_3 + H_2O.$$

Hydroxyl derivatives of the members of Group VI corresponding to the general formula $R(OH)_6$ are known, as, for example, the so-called hydrate of sulphuric acid, $S(OH)_6$. The maximum hydroxides of Group VII should have the general formula $R(OH)_7$, but those known do not correspond to this. The nearest approach to it is found in crystallized periodic acid, $H_5IO_6$, which may be

regarded as derived from the hydroxide $I(OH)_7$ by loss of one molecule of water, thus :

$$I(OH)_7 = OI(OH)_5 + H_2O.$$

The arrangement of Lothar Meyer is a continuous one. The elements are arranged on a spiral beginning with lithium and ending with uranium. The divisions are such that when the two ends of the table are brought together on a cylinder, the line ending with fluorine will join that beginning with sodium ; that ending with nickel will join that beginning with copper ; and so on. In other respects the arrangement is much like that in Mendeléeff's Table I. What Mendeléeff calls a Group, Lothar Meyer calls a *Natural Family*, while those elements which fall in the same horizontal line are said to form a series. Now, each natural family falls into two groups indicated by the letters A and B placed above. Thus the first natural family falls into Group A, consisting of lithium, sodium, potassium, rubidium, and cæsium, and Group B, consisting of copper, silver, and gold. Family II falls into Group A, consisting of glucinum, magnesium, calcium, strontium, barium, and perhaps erbium, and Group B, consisting of zinc, cadmium, and mercury ; etc. The members of each group in a family resemble one another much more closely than they resemble the members of the other group.

The figures at the bottom of the table of Lothar Meyer refer to the valence of the elements in each group. Judging by the composition of the oxides and hydroxides, the valence increases from 1 to 8 from Families I to VIII. But the valence of the elements in each family varies according to conditions. Thus the valence of the elements of Family IV is generally 4, as shown in the compounds $CH_4$, $CCl_4$, $CO_2$, $SiH_4$, $SiCl_4$, $SiO_2$, etc. ; but they may also appear as bivalent elements, as seen in the compound $CO$. So too, while the elements of Family V are quinquivalent, as in $PCl_5$, $NH_4Cl$, etc., they may also be trivalent, as in $PCl_3$, $NH_3$, etc.

What we call valence does not then appear to be an

unchangeable property of the elements, but a property
which may change according to conditions.  It appears
further that a given element may have one valence tow-
ards one element and another valence towards another
element.   This is most strikingly seen on comparing
the formulas of the hydrogen compounds of the ele-
ments of Families V, VI, and VII with those of their
oxygen compounds.   The members of Family VII com-
bine with hydrogen in only one proportion, and that is
the simplest possible.   Towards hydrogen these elements
are univalent, and their valence towards hydrogen is con-
stant.   On the other hand, they combine with oxygen
and with hydroxyl in several proportions, and judging by
the composition of these compounds, the valence tow-
ards oxygen varies from 1 to 7.   The members of
Family VI are bivalent towards hydrogen, and their hy-
drogen valence is constant; but they combine with oxy-
gen and hydroxyl in several proportions, and the compo-
sition of the compounds indicates that their valence
towards oxygen varies from 2 to 6.   The hydrogen val-
ence of the members of Family V is 3, while the oxygen
valence varies from 1 to 5.   Finally, the hydrogen val-
ence of the members of Family IV is 4, while the oxygen
valence varies from 2 to 4.   As regards the hydrogen
valence of the members of Families I to III, but little is
known.   These elements do not generally combine with
hydrogen, though some of them do.   Towards oxygen
their valence is fairly constant, though some variations
are observed as in the case of copper and mercury.

   Judging then by the composition of the compounds,
we are justified in making a distinction between the
*hydrogen-valence* of some elements and their *oxygen-
valence*.   While the former is constant, the latter is sub-
ject to variations.   In those cases in which there is a
marked difference between the *hydrogen-valence* of an ele-
ment and its maximum *oxygen-valence*, the maximum
valence towards chlorine is greater than the hydrogen-
valence and less than the maximum oxygen-valence.
This is shown in the case of sulphur; the formulas of its

hydrogen compound and of its highest compounds with chlorine and oxygen being respectively

$$SH_2, \qquad SCl_4, \qquad SO_3.$$

From this it appears that the maximum valence of sulphur towards hydrogen is 2, towards chlorine 4, and towards oxygen 6.

**Connection between the Position of the Elements in the Natural System and their Chemical Properties.**—The changes in composition of the oxygen and hydrogen compounds and of the hydroxides from Family I to VII have been referred to. Another fact of great importance is that the elements of Group I are the most strongly marked base-forming elements, while those of Group VII are the most strongly marked acid-forming elements. Passing in either direction the character of the elements becomes less pronounced, until in the middle (Group IV), elements which form neither strongly marked acids nor strongly marked bases are found. Thus, beginning with sodium, this element forms a strong base, magnesium forms a weaker base, the hydroxide of aluminium is a still weaker base. Beginning, on the other hand, with chlorine at the other end of the same series, its hydrogen compound is a strongly marked acid ; that of sulphur is an acid, but less marked in character than hydrochloric acid ; that of phosphorus has no acid properties, nor has that of silicon. The hydroxides of these four elements have acid properties. Each one, however, forms several acids, and it is difficult to compare them, as some of those of chlorine are strongly marked and others not, as we have seen.

Some very interesting variations in properties are also noticed in passing from one end of a group of a natural family to the other. Thus in Group B, Family VII, the activity of the elements grows less from fluorine to iodine, or, as we commonly say, fluorine is the strongest element in the group, and then follow, in order, chlorine, bromine, and iodine.

The remarkable relations above referred to are summed up in the periodic law :

*The properties of an element are periodic functions of the atomic weight.*

It appears that if an element has a certain atomic weight it must have certain properties, and that if the atomic weight is known the properties can be stated, just as, if the properties are known, the atomic weight can be approximately stated. When the law was first stated, Mendeléeff predicted the discovery of certain elements to fill some of the vacant places in the table. At that time the elements gallium, Ga, scandium, Sc, and germanium, Ge, were not known. Not only was their discovery predicted, but their properties were clearly stated years before they were brought to light. Within the last few years these three elements have been discovered, and a remarkable agreement is observed between their properties as determined by observation and as foretold by Mendeléeff by the aid of the periodic law.

The relations between the atomic weights and properties will appear more and more clearly as our study of the elements proceeds. The natural arrangement of the elements suggested by the periodic law is adopted in this book. The elements hydrogen, oxygen, and chlorine were studied at the outset in order to illustrate the methods of studying chemical problems, and as examples of chemical elements in general. It is, however, now time to take up the elements systematically, and to learn what may be necessary in regard to them in order to get as clear a notion as possible of the facts and principles of the science of chemistry.

**Plan to be followed.**—The most systematic method of procedure in studying the elements would be to begin with Family I, Group A (see Lothar Meyer's Table, p. 151), then to take up Group B of the same family ; and so on in order, ending with Family VIII. It seems better, however, to begin with Family VII ; to follow with Families VI, V, and IV ; and then to take up in order Families I, II, III, and VIII. The main reason

for this is that it is impossible to study most of the members of Families I, II, III, and VIII without a knowledge of several of the elements of Families VII, VI, V, and IV, while these last families can be studied with only slight reference to the others. It is proposed then to begin with Group B, Family VII, the members of which are very much like chlorine. The only member of Group A of this family is manganese. While manganese resembles the members of the chlorine group in some respects, it has other properties which ally it to the so-called base-forming elements. So also the members of Group A, Family VI, are like the members of the oxygen or sulphur group, but they are also allied to the base-forming elements. A similar difference is observed between the members of Groups A and B, Family V.

While the plan above sketched takes into consideration the greater number of the analogies of the elements, there are other analogies which are not brought out. Thus, as will be seen in due time, the elements aluminium, chromium, manganese, and iron are analogous in some respects, but by following the plan sketched they will be taken up in different groups. This appears to be justified, however, when we consider the entire conduct of these elements, and do not confine ourselves to a study of only a few reactions which, being useful for some purposes, have been studied more carefully than others which from a scientific point of view are perhaps just as important.

# CHAPTER XII.

**General.**—The elements of this group are commonly called the *halogens*. The best known member of the group is chlorine, which has already been treated. Although fluorine is in general like the other members of the group, it differs from them in some respects, and it certainly is not as much like them as they are like one another. While chlorine, bromine, and iodine accompany one another in nature, fluorine compounds are not generally found in company with compounds of the other elements of the family. In those cases in which chlorine, bromine, and iodine are found together, chlorine is generally present in largest quantity, and iodine in smallest quantity. Fluorine and chlorine are gases under ordinary conditions, while bromine is a liquid and iodine is a solid. Fluorine, bromine, and iodine form with hydrogen the compounds hydrofluoric acid, $HF$, hydrobromic acid, $HBr$, and hydriodic acid, $HI$, which are analogous to hydrochloric acid. All these compounds are gases which have marked acid properties. With oxygen, fluorine does not combine, whereas chlorine, bromine, and iodine combine with it in a number of proportions, as has already been seen in the case of chlorine. Among themselves these elements also form some compounds: thus bromine and chlorine form the compound $BrCl$; iodine forms the compounds $ICl$, $ICl_3$, $IBr$, and $IF_5$. It appears from this that the valence of iodine towards bromine is 1, towards chlorine 3, and towards fluorine 5.

Towards base-forming members the elements of this group are univalent, as shown in such compounds as $NaCl$, $KBr$, $CaCl_2$, $KI$, etc. They, however, appear to

have a valence greater than 1 in some compounds known as double salts. These can be explained satisfactorily only by assuming that in them the element is in combination with itself and has a valence greater than 1.

## BROMINE, Br (At. Wt. 79.34).

**Occurrence.**—This element occurs in nature in company with chlorine. Chlorine, as has been stated, occurs mostly in combination with sodium, as sodium chloride, or common salt. In several of the great salt-beds bromine occurs in the form of sodium bromide, NaBr, and in some places it occurs as magnesium bromide, $MgBr_2$. The chief source of bromine is the mother-liquors from the salt works. When a solution containing a large quantity of sodium chloride and a small quantity of bromide is evaporated, the chloride is first deposited, and from the mother-liquors the bromide mixed with chloride is deposited. The great beds at Stassfurt are particularly rich in bromides, and a great deal of bromine is made from the salts which occur in this locality.

**Preparation.**—Bromine can be prepared from **the** bromides in the same way that chlorine is made from the chlorides: by first treating with sulphuric acid, thus liberating hydrobromic acid, and then treating with manganese dioxide, or, better, by mixing the bromide with manganese dioxide and treating the mixture with sulphuric acid. The reaction is represented by the equation

$$2NaBr + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

Or it may be represented as taking place in different stages. First the sulphuric acid would liberate hydrobromic acid from the bromide, and this would act upon the manganese dioxide thus:

$$MnO_2 + 4HBr = MnBr_2 + 2H_2O + Br_2.$$

But sulphuric acid would act upon manganous bromide, $MnBr_2$, thus:

$$MnBr_2 + H_2SO_4 = MnSO_4 + 2HBr;$$

and the hydrobromic acid would then again react with manganese dioxide, etc.

Another method for the preparation of bromine depends upon the fact that chlorine has the power to set bromine free from its compounds. If, therefore, a solution containing a bromide is treated with manganese dioxide and hydrochloric acid, the chlorine which is formed from the hydrochloric acid will act upon the bromide and bromine will be given off. This method is used at Stassfurt.

**Properties.**—Bromine is a heavy, dark-red liquid at ordinary temperatures. If exposed to the air it is converted into a vapor of a brownish-red color. It boils at 58–58.6°, and at − 7.3° it is solid. It has an extremely disagreeable odor, to which fact it owes its name (from βρωμος, a stench). From carbon disulphide at − 90° it crystallizes in fine dark-red needles.

Its properties are similar to those of chlorine. It acts violently upon organic substances ; attacking the skin, and the membranes lining the passages of the throat and lungs. Wounds caused by the liquid coming in contact with the skin are painful and serious, and it must therefore be handled with great care.

Like chlorine, bromine is dissolved by water, one part dissolving in 33.3 parts at 15°. The solution, which has a reddish color and the odor of bromine, is called *bromine water*. At a low temperature bromine forms with water a compound in every way analogous to chlorine hydrate, *viz.*, bromine hydrate, $Br_2 + 10H_2O$. This decomposes when left in contact with the air at ordinary temperatures.

**Chemical Conduct of Bromine.**—Bromine acts chemically like chlorine. It was pointed out that chlorine acts in three different ways : (1) By direct addition ; (2) by substitution ; and (3) by liberating oxygen from water, as in bleaching and other oxidizing processes. Bromine is capable of acting in all three ways. It combines directly with base-forming elements or metals, as iron, aluminium, potassium, etc. ; also with the acid-forming elements, as sulphur, phosphorus, etc. It com-

bines with hydrogen almost as readily as chlorine does. With oxygen it does not combine directly, and in this respect also it is like chlorine.

It acts upon compounds containing hydrogen almost as readily as chlorine does, replacing the hydrogen and forming bromine substitution-products. Thus benzene, $C_6H_6$, yields the products $C_6H_5Br$, $C_6H_4Br_2$, $C_6H_3Br_3$, $C_6H_2Br_4$, etc., and the hydrogen which leaves the compound passes off in combination with bromine in the form of hydrobromic acid.

It bleaches like chlorine, partly by direct action and disintegration of the organic dye-stuffs, partly by action upon water, liberating oxygen.

A solution of bromine in water left exposed to the direct sunlight loses its color and becomes acid in consequence of the decomposition of the water, as in the case of chlorine :

$$Br_2 + H_2O = 2HBr + O,$$

$$\text{or} \quad 2Br_2 + 2H_2O = 4HBr + O_2.$$

**Uses of Bromine.**—Bromine and its compounds are used in photography, medicine, and to some extent in the manufacture of coal-tar colors. It is manufactured in large quantity, and a good proportion of it is manufactured in the United States. According to the official report the production of bromine in the United States in the year 1896 amounted to over 500,000 pounds.

**Hydrobromic Acid, HBr.**—The only compound which bromine forms with hydrogen alone is hydrobromic acid. This is in all respects very much like hydrochloric acid. It is set free from bromides by the action of sulphuric acid, but owing to its instability it acts upon the sulphuric acid, causing decomposition. The elements hydrogen and bromine are not held together as firmly in hydrobromic acid as hydrogen and chlorine are in hydrochloric acid. Consequently, if hydrobromic acid is brought together with certain substances which contain oxygen it gives up its hydrogen to the oxygen. This is

seen in the conduct towards manganese dioxide. But towards this substance both hydrochloric and hydrobromic acids act in essentially the same way. Sulphuric acid does not, however, give up its oxygen as readily as manganese dioxide, and the difference in the stability of the hydrogen compounds of chlorine and bromine is seen very clearly in their conduct towards sulphuric acid. Hydrochloric acid does not act upon sulphuric acid at all. Hydrobromic acid acts according to the following equation :

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

The action consists in the decomposition of the hydrobromic acid into bromine and hydrogen, and the subsequent action of the nascent hydrogen upon the sulphuric acid thus :

$$2HBr = 2H + Br_2 ; \text{ and}$$

$$H_2SO_4 + 2H = 2H_2O + SO_2.$$

The hydrobromic acid acts here, then, as a reducing agent, and the sulphuric acid as an oxidizing agent. It is plain that hydrobromic acid cannot be made in pure condition by the action of sulphuric acid upon a bromide. Some of the hydrobromic acid, to be sure, escapes the action of the sulphuric acid, but at best it is always mixed with the compound $SO_2$, or sulphur dioxide, which is a gas, and with bromine.

It can be made by passing a mixture of hydrogen and bromine over heated finely divided platinum. An apparatus has been devised for making hydrobromic acid in this way in quantity.

It can also be made by allowing bromine to act upon an organic compound containing hydrogen. Substituting action takes place and hydrobromic acid is given off. Thus, if a compound of the formula $C_{10}H_{22}$ were used, the reaction would be represented in this way :

$$C_{10}H_{22} + Br_2 = C_{10}H_{21}Br + HBr.$$

The product $C_{10}H_{21}Br$, or the bromine substitution-product, would not be volatile at ordinary temperatures, and therefore only the hydrobromic would be given off.

The method most commonly adopted in the laboratory consists in treating phosphorus with bromine and water. In all probability the bromine acts first upon the phosphorus, forming the product $PBr_3$ or $PBr_5$ according to the proportions of the substances used. Both these substances are decomposed by water, the first forming phosphorous acid and hydrobromic acid, according to this equation:

$$P \begin{cases} Br & HHO \\ Br + HHO = PO_3H_3 + 3HBr, \\ Br & HHO \end{cases}$$

or  $PBr_3 + 3H_2O = PO_3H_3 + 3HBr$ ;

the second forming phosphoric acid and hydrobromic acid :

$$PBr_5 + 4H_2O = PO_4H_3 + 5HBr.$$

The gas thus formed can be freed from bromine by passing it through a tube containing phosphorus.

**Properties.**—Hydrobromic acid is a colorless gas which forms fumes in contact with the air in consequence of its attraction for moisture. It dissolves in water in large proportion. The solution conducts itself much like hydrochloric acid. When boiled a compound of definite composition passes over under ordinary conditions. It corresponds to the formula $HBr + 5H_2O$, but here, as with the hydrate of hydrochloric acid, the composition changes with the pressure. With metallic hydroxides or bases, hydrobromic acid forms bromides, as hydrochloric acid forms chlorides :

$$KOH + HBr = KBr + H_2O.$$

**Compounds of Bromine with Hydrogen and Oxygen.**—With hydrogen and oxygen bromine forms compounds which closely resemble those which chlorine forms with the same elements. They are : Hypobromous acid,

HBrO; bromic acid, $HBrO_3$; and perhaps perbromic acid, $HBrO_4$.

*Hypobromous acid,* HBrO, is made by reactions which are entirely analogous to those used in making hypochlorous acid. When bromine acts upon a dilute solution of sodium or potassium hydroxide, reaction takes place thus:

$$2KOH + Br_2 = KBr + KBrO + H_2O.$$

So also bromine vapor acting upon slaked lime or calcium hydroxide forms a compound similar to bleaching powder. Hypobromous acid has not been prepared in pure condition owing to its instability.

*Bromic acid,* $HBrO_3$, is not known in pure condition. Its salts are made in the same way as the chlorates are; the principal reaction made use of for the purpose being that between bromine and concentrated potassium hydroxide:

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

The decompositions of the bromates are much like those of the chlorates.

As regards the existence of perbromic acid there is some doubt. It is stated by one observer that he obtained it by treating perchloric acid with bromine:

$$HClO_4 + Br = HBrO_4 + Cl.$$

Others have not succeeded in getting it in this or in any other way.

**Compound of Bromine and Chlorine.**—When chlorine is passed into liquid bromine it is absorbed in large quantity. If the process is carried on at a low temperature the product BrCl is formed. Above 10° it undergoes decomposition. Although it is unstable, there is no good reason for regarding this substance as anything but a chemical compound. There are many chemical compounds known which are less stable than this.

## Iodine, I (At. Wt. 125.89).

**Occurrence.**—Iodine, as has already been stated, occurs in company with chlorine and bromine in nature, but in smaller quantity than these. The relative quantity in sea water is extremely small. The sea plants, however, assimilate it, and the ashes of these plants contain a considerable quantity of compounds of iodine. It also occurs in small quantity in the great beds of soda salt-peter, or sodium nitrate, which are found in Chili, South America. It occurs in small quantity in combination with silver, and also in combination with lead and with mercury.

**Preparation.**—The method of obtaining iodine from its salts is like that used in making chlorine and bromine from the chlorides and bromides. It consists in treating the iodides with sulphuric acid and manganese dioxide.

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

The iodine, although solid at the ordinary temperature, is easily volatilized, and if the mixture mentioned is heated, iodine vapor passes over and may be condensed in appropriately arranged vessels.

On the large scale iodine is obtained mostly from sea-weed. On the coasts of Scotland, Ireland, and France the sea-weed which is thrown up by storms is gathered, dried, and burned. The organic portions are thus destroyed, and the mineral or earthy portions are left behind as ashes. This incombustible residue is called *kelp*. It contains a small percentage of potassium iodide, from .5 to 2 per cent according to the sea-weed used. The dried weed was formerly burned in cavities dug in the earth, but of late years the process has in some places been much improved, and the yield in kelp increased.

In Scotland the iodine is liberated by means of sulphuric acid and manganese dioxide. In France, how-

ever, this is effected by passing chlorine into the solution containing the iodide. If too little chlorine is used all the iodine is not separated ; if too much, a compound of iodine and chlorine is formed, or an iodate, in consequence of the oxidizing action of the chlorine on the iodine.

The iodine which occurs in Chili saltpeter, $NaNO_3$, is in the form of sodium iodate, $NaIO_3$, and iodide, $NaI$, and to some extent as magnesium iodide, $MgI_2$. Most of the iodine now in the market is made from this material, and the competition created in this way has led to a careful study of the process for obtaining iodine from kelp. Sea-weed is now collected from certain parts of the ocean where it grows in large quantity, vessels being sent out for the purpose.

**Properties.**—Iodine is a grayish-black crystallized solid. At ordinary temperatures it is volatile. According to the most reliable determinations it melts at 113–115°, and boils at 250°. The vapor has a violet color when mixed with air. When in pure condition it is intensely blue. At temperatures considerably above the boiling point the specific gravity of iodine vapor is such as to show that its molecular weight is approximately 254, or twice the atomic weight. As the temperature is raised, however, the specific gravity is lowered, until, finally, at a very high temperature, it becomes about half what it is at lower temperatures. This is accounted for by supposing that at the lower temperatures the molecules of iodine consist of two atoms each, while as the temperature is raised these molecules are gradually broken down, so that at the temperature at which the lowest specific gravity is reached the iodine vapor consists of free atoms, or the atoms and molecules are then identical, and the specific gravity is therefore only half what it is when the molecules consist of two atoms.

Iodine has a characteristic strong taste. It acts upon the mucous membranes, but much less energetically than chlorine or bromine. It colors the skin yellowish-

brown, and acts as an absorbent, causing the reduction of some kinds of swellings.

It dissolves slightly in water, easily in alcohol, and easily in a water solution of potassium iodide. The solution in alcohol is known as tincture of iodine. It dissolves also in carbon disulphide, $CS_2$, and in chloroform forming solutions which have a beautiful deep violet color.

In general, iodine conducts itself chemically like bromine and chlorine, only it acts in almost all reactions less energetically than the other two elements. It combines directly with a number of elements, as with hydrogen, sulphur, phosphorus, iron, mercury, etc. In presence of water it acts as an oxidizer just as chlorine and bromine do, but less energetically. Thus it oxidizes sulphurous acid, $H_2SO_3$, to sulphuric acid, $H_2SO_4$:

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

As a substituting agent it does not act as readily as chlorine and bromine, though iodine substitution-products are made in large quantities, particularly in connection with the manufacture of dye-stuffs.

Iodine is used extensively in the dye-stuff industry, in photography, and in medicine. One factory in Scotland makes on an average 60 tons of iodine a year.

**Hydriodic Acid, HI.**—The affinity of hydrogen for iodine is less than for bromine, and therefore hydriodic acid cannot be made pure by treating an iodide with sulphuric acid. The hydrogen of the hydriodic acid acts upon the sulphuric acid very readily, and according to the conditions the following reactions may take place:

$$H_2SO_4 + 8HI = 4H_2O + SH_2 + 4I_2;$$
$$H_2SO_4 + 6HI = 4H_2O + S + 3I_2;$$
$$H_2SO_4 + 2HI = 2H_2O + SO_2 + I_2.$$

On treating potassium iodide with sulphuric acid, therefore, there may be formed, in addition to hydriodic

acid and free iodine, sulphur dioxide, sulphur and hydrogen sulphide.

The method adopted for the preparation of hydriodic acid is like that used for the preparation of hydrobromic acid. It consists in treating phosphorus with iodine and water. The reactions involved are of the same kind as those which were discussed under hydrobromic acid. The iodine probably acts at first on the phosphorus, forming a compound of phosphorus and iodine, which then in turn is decomposed by the water. The reactions which generally take place are those represented by the following equations :

$$P \quad + 3I \quad = PI_3 ;$$
$$PI_3 + 3H_2O = PO_3H_3 + 3HI.$$

Hydriodic acid is a colorless transparent gas like hydrochloric and hydrobromic acids. It also like these dissolves in water in large quantity, and when brought in contact with the air it forms dense white fumes. When boiled the water solution conducts itself like those of hydrochloric and hydrobromic acids. The liquid, which boils at 127° under the ordinary atmospheric pressure, contains 57 per cent hydriodic acid. If the solution of the gas in water is allowed to stand, decomposition begins in consequence of the action of the oxygen of the air. The hydrogen is oxidized to water and the iodine is set free, coloring the solution brown.

When heated, the gas begins to decompose at 180°, and at higher temperatures the decomposition takes place rapidly. The products are simply hydrogen and iodine. In consequence of the ease with which hydriodic acid breaks down, yielding free hydrogen, it is an excellent reducing agent, and it is frequently used in the laboratory for the purpose of extracting oxygen from substances. Its action upon sulphuric acid has already been spoken of. The reason why it acts so well is that the hydrogen is separated from the iodine with little expenditure of energy, and the hydrogen thus separated is in the nascent state, or, as is believed, in the atomic state.

**Iodic Acid, $HIO_3$.**—This compound is strictly analogous to chloric and bromic acids, but differs from them in being much more stable. It can be made by treating iodine with strong oxidizing agents, as, for example, concentrated nitric acid. It is also formed very easily by passing chlorine through water in which iodine is suspended, when hydrochloric acid and iodic acid are formed, as represented in this equation :

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

The reaction is probably somewhat more complicated than it appears from this equation, for when chlorine acts upon iodine a compound of the two elements is first formed. Iodine trichloride is decomposed by water thus :

$$2ICl_3 + 3H_2O = 5HCl + HIO_3 + ICl.$$

Iodine monochloride is also decomposed by water, giving iodic acid, hydrochloric acid, and free iodine :

$$10ICl + 6H_2O = 10HCl + 2HIO_3 + 4I_2.$$

Whether these chlorides of iodine are formed or not, the prime causes of the formation of iodic acid when chlorine acts upon iodine in water are the oxidizing power of the chlorine and the affinity of iodine for oxygen.

When iodine is dissolved in an alkali the reaction which takes place is the same as that which takes place with chlorine and bromine under like circumstances. A mixture of the iodide and iodate is formed :

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Iodic acid is a crystallized solid, which when heated to 170° loses water and is converted into iodine pentoxide, $I_2O_5$ :

$$2HIO_3 = I_2O_5 + H_2O.$$

Its salts have the general formula $MIO_3$, though it also forms salts $MH(IO_3)_2$ and $MH_2(IO_3)_3$. It gives up its oxygen readily and is therefore a good oxidizing agent, just as hydriodic acid is a good reducing agent.

**Iodine Pentoxide or Iodic Anhydride, $I_2O_5$.**—This compound is formed, as was stated in the last paragraph, by heating iodic acid to 170°. It is a white solid which is easily soluble in water, forming iodic acid. It is decomposed when heated to 300°. It will be observed, therefore, that this compound of iodine and oxygen is very much more stable than any of the compounds of chlorine or bromine and oxygen ; and it is interesting to note that as the affinity for oxygen increases, that for hydrogen decreases. In the group chlorine, bromine, and iodine, chlorine has the strongest affinity for hydrogen and the weakest for oxygen, while iodine has the strongest affinity for oxygen and the weakest for hydrogen. We shall presently see that fluorine, which does not unite with oxygen, has a stronger affinity for hydrogen than chlorine has.

**Anhydrides, or Acidic Oxides.**—An oxide which, like iodine pentoxide, forms an acid when dissolved in water, or which forms salts by treatment with basic hydroxides, is called an *anhydride* or *acidic oxide*. The oxides of the base-forming elements form bases when dissolved in water, and they are, therefore, called *basic oxides*. As examples of acidic oxides or anhydrides, there may be mentioned besides iodic anhydride, sulphuric anhydride, $SO_3$ ; sulphurous anhydride, $SO_2$ ; phosphoric anhydride, $P_2O_5$ ; carbonic anhydride, $CO_2$. When dissolved in water these oxides are converted into acids as represented in these equations :

$$SO_3 + H_2O = H_2SO_4 ;$$
$$SO_2 + H_2O = H_2SO_3 ;$$
$$P_2O_5 + H_2O = 2HPO_3 ;$$
$$CO_2 + H_2O = H_2CO_3.$$

Silicic anhydride, $SiO_2$, is an example of an acidic oxide which does not dissolve in water, but which does form salts when treated with basic hydroxides :

$$SiO_2 + 2KOH = K_2SiO_3 + H_2O.$$

As examples of basic oxides or oxides which when treated with water yield bases, the following may be taken: calcium oxide, $CaO$; potassium oxide, $K_2O$; barium oxide, $BaO$. As has already been shown, when treated with water these are respectively converted into calcium hydroxide, $Ca(OH)_2$; potassium hydroxide, $KOH$; and barium hydroxide, $Ba(OH)_2$. There are, however, many basic oxides which do not dissolve in water, but which, nevertheless, have the power to neutralize acids and form salts. This is true, for example, of aluminium oxide, $Al_2O_3$, lead oxide, $PbO$, manganous oxide, $MnO$, cupric oxide, $CuO$, etc. The action of such oxides upon acids takes place as represented below:

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O\ ;$$
$$PbO\ + 2HNO_3 = Pb(NO_3)_2 + H_2O\ ;$$
$$MnO + 2HCl\ \ = MnCl_2\ \ \ + H_2O\ ;$$
$$CuO\ + H_2SO_4\ = CuSO_4\ \ + H_2O.$$

**Periodic Acid, $H_5IO_6$.**—This acid is analogous to perchloric acid. Its salts are formed by oxidation of iodates or by heating iodates, just as perchlorates are formed by heating chlorates. The simplest way to make a periodate is to pass chlorine into a solution containing sodium hydroxide and sodium iodate, when a reaction takes place which is at least partly represented by the following equation:

$$NaIO_3 + 3NaOH + Cl_2 = Na_2H_3IO_6 + 2NaCl.$$

The salt $Na_2H_3IO_6$ is difficultly soluble in water, and therefore separates from the solution. From the sodium salt the corresponding silver salt, $Ag_2H_3IO_6$, can be obtained, and when this silver salt is treated with nitric acid it is converted into the simpler salt, $AgIO_4$, which is evidently derived from the simpler acid, $HIO_4$:

$$2Ag_2H_3IO_6 + 2HNO_3 = 2AgNO_3 + 4H_2O + 2AgIO_4.$$

The acid when separated from its solutions is a crystallized solid which has the composition $H_5IO_6$. When heated it undergoes decomposition, losing water and oxygen, and yielding iodic acid. It cannot, however, be converted into a compound of the composition $HIO_4$, for the loss of water is always accompanied by a loss of oxygen. Like iodic acid, periodic acid is a good oxidizing agent in consequence of the ease with which it gives up its oxygen.

**Periodates.**—Periodic acid yields a large number of salts the connection between which and the acid does not appear clear at first sight. A few examples will suffice for the present purpose : $KIO_4$, $Na_5IO_6$, $Ag_3IO_5$, $Ag_4I_2O_9$, $Zn_4I_2O_{11}$.

**Constitution of Periodic Acid.**—The complicated salts of periodic acid are apparently inexplicable on any other theory than that they are derived from acids which are closely related to the hypothetical acid $I(OH)_7$. This is now commonly regarded as *normal periodic acid*. It, however, breaks down into the ordinary form of the acid by loss of water. The relation is expressed thus :

$$I\begin{cases} OH \\ OH \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases} = I\begin{cases} O \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases} + H_2O.$$

The salts $Na_2H_3IO_6$, $Na_5IO_6$, and others of the same kind are derived from this acid by replacement of one or more of the hydrogen atoms by metallic elements. The acid of the formula $H_5IO_6$ can also be imagined to break down into $H_3IO_5$ and water thus :

$$I\begin{cases} O \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases} = I\begin{cases} O \\ O \\ OH \\ OH \\ OH \end{cases} + H_2O.$$

The salt $Ag_3IO_5$ and similar known salts are plainly derived from this hypothetical acid $H_3IO_5$. Finally, the acid $H_3IO_5$ can also be imagined to break down into $HIO_4$ and water thus :

$$\mathrm{I}\begin{cases} O \\ O \\ OH \\ OH \\ OH \end{cases} = \mathrm{I}\begin{cases} O \\ O \\ O \\ OH \end{cases} + H_2O \,;$$

and the salts like $KIO_4$ are derived from this hypothetical acid. It appears, therefore, that the assumption of the fundamental normal acid, $I(OH)_7$, is competent to explain the existence of the salts which are derived from the acids $H_5IO_6$, $H_3IO_5$, and $HIO_4$. More complicated acids can be formed by the loss of water from two or more molecules of any one of these simpler acids. Thus, if from two molecules of the acid $H_3IO_5$ one molecule of water is taken, an acid of the formula $H_4I_2O_9$ would be formed ; or if two molecules of the acid $H_5IO_6$ lose one molecule of water, the acid $H_8I_2O_{11}$ would be formed. These relations are made clear by the equations here given :

$$2\mathrm{I}\begin{cases} O \\ O \\ OH \\ OH \\ OH \end{cases} = (HO)_2O_2I\text{--}O\text{--}IO_2(OH)_2 + H_2O \,;$$

$$2\mathrm{I}\begin{cases} O \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases} = (HO)_4OI\text{--}O\text{--}IO(OH)_4 + H_2O$$

A salt of the formula $Ag_4I_2O_9$, and another of the formula $Zn_4I_2O_{11}$, are known. The former is derived from the acid $H_4I_2O_9$, the latter from the acid $H_8I_2O_{11}$, by the substitution of four bivalent atoms of zinc for the eight atoms of hydrogen. There are many more complicated

salts than those mentioned, but they can all be satisfactorily explained by the assumption that they are related to the normal acid I $(OH)_7$, in which iodine is septivalent. The existence of the periodates, the ease with which they can be explained by the above method, and the apparent impossibility of explaining them on the assumption that iodine is univalent, form an exceedingly strong argument in favor of the view that iodine is septivalent in these compounds.

**Constitution of Iodic Acid and the Oxygen Acids of Bromine.**—The conclusion reached in regard to the constitution of periodic acid makes it appear highly probable that perchloric acid has a similar constitution, and this view is now commonly accepted, as was stated when the acid was discussed. Applying a similar method to iodic acid, it appears probable that this is derived from the acid I$(OH)_5$ by loss of water :

$$I(OH)_5 \ = \ IO_2(OH) + 2H_2O \ ; \ or$$

$$I \begin{cases} OH \\ OH \\ OH \\ OH \\ OH \end{cases} = \ I \begin{cases} O \\ O \\ OH \end{cases} + 2H_2O.$$

The iodine is regarded as quinquivalent in both forms of the acid. This is represented in the case of the acid $O_2I(OH)$ by the structural formula

$$\underset{\overset{|}{OH}}{O=I=O}$$

The corresponding compound of bromine is regarded as having the same constitution as the iodine compound.

**Compounds of Iodine with Chlorine.**—When chlorine is passed over dry crystallized iodine it is absorbed, and a compound of the formula ICl is formed. This is a thick reddish-brown, very volatile liquid. Under proper conditions it solidifies in crystals. Iodine chloride is decomposed by water, the products being iodic acid, hydro-

chloric acid, and free iodine, as stated under Iodic Acid (p. 171).

If the passage of chlorine over iodine is continued beyond the point required for the formation of the simple compound ICl, the trichloride $ICl_3$ is formed. This is a crystallized compound of a yellow color. When heated it breaks down into chlorine and iodine monochloride. When treated with water it is partly dissolved without decomposition, but it is partly decomposed, yielding iodic acid, iodine monochloride, and hydrochloric acid.

**Compound of Iodine with Bromine.**—There is only one compound of iodine and bromine known, and that is the one having the formula IBr. It is a crystallized compound which is formed by direct combination of the two elements. It is decomposed by heat and by water.

## FLUORINE, F (At. Wt. 18.91).

**Occurrence.**—This element occurs in large quantity in nature, and is widely distributed, but it is always in combination with other elements. It is found chiefly in combination with calcium, as *fluor-spar* or *calcium fluoride*, $CaF_2$, and in combination with sodium and aluminium, as *cryolite*, a mineral which occurs abundantly in Greenland and has the composition represented by the formula $Na_3AlF_6$ or $AlF_3.3NaF$. It is called fluorine from the fact that it occurs in fluor-spar, which in turn receives its name for the reason that it melts when heated and is therefore used as a flux in heating chemical substances together (from *fluo*, I flow). On account of the remarkable affinity of fluorine for other elements, all attempts to prepare it in the free condition failed until a few years ago, when its isolation was effected by passing an electric current through liquid hydrofluoric acid contained in a platinum vessel.

**Properties.**—Fluorine is a light greenish-yellow gas, that has recently been converted into a liquid at a very low temperature. It acts upon almost all substances. Thus, it decomposes water, yielding ozone and hydrofluoric acid ; it combines directly with hydrogen at the ordinary

temperature; and with sulphur, phosphorus, iron, etc., with evolution of light and heat. It does not, however, act upon platinum. Owing to its active properties it is of course a difficult matter to isolate and preserve it.

**Hydrofluoric Acid, HF.**—Hydrofluoric acid is made by treating a fluoride with sulphuric acid. Thus, when calcium fluoride or fluor-spar is used, this reaction takes place :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The reaction must be performed in vessels of platinum or lead, as glass is disintegrated by the acid. In perfectly pure anhydrous condition it can be obtained by heating the pure dry salt $KHF_2$, known as acid potassium fluoride. It is a liquid which boils at $19.4°$ and does not solidify even at a very low temperature. The pure dry acid in the liquid form does not act upon glass. It does not dissolve the acid-forming elements, but does dissolve most of the base-forming elements with evolution of hydrogen and formation of fluorides. The gas acts upon the skin, causing swellings and violent pains. Inhaled it is poisonous. To preserve it, vessels of platinum or caoutchouc must be used. In the moist condition it attacks glass, converting the silicon into the fluoride, $SiF_4$, and the metals into their fluorides. A silicate of the formula $CaSiO_3$ would undergo the changes represented in the following equation :

$$CaSiO_3 + 6HF = CaF_2 + SiF_4 + 3H_2O.$$

Silicon fluoride is a gas, and calcium fluoride is soluble in acids. Thus calcium silicate, which is insoluble in water, is so changed by hydrofluoric acid as to be rendered soluble. In a similar way glass, which is a compound resembling calcium silicate, is rendered soluble, or is, as we commonly say, dissolved, by hydrofluoric acid.

When an aqueous solution of hydrofluoric acid is boiled it passes over at $120°$, and the distillate contains 36 to 38 per cent of the acid.

Hydrofluoric acid is used for the purpose of etching glass, particularly for marking scales on thermometers and other graduated glass instruments. The glass is covered with a thin layer of wax or paraffin and, at the places where the etching is wanted, marks are made through the paraffin, so that the glass is exposed. Those parts of the glass which are covered are not acted upon by the hydrofluoric acid, while those parts which are not covered are corroded and, when the paraffin is removed, permanent marks are found corresponding to those made through the paraffin. A solution of hydrofluoric acid in water is manufactured and sold in rubber bottles.

The specific gravity of hydrofluoric acid gas at about 100° leads to the molecular weight corresponding to the formula HF, fluorine having the atomic weight 19. At about 30° the specific gravity corresponds to the formula $H_2F_2$. At lower temperatures the molecular weight appears to be still greater. In solutions of ordinary concentration in water the substance appears to have the formula $H_2F_2$, while when the solution is much diluted the formula becomes HF.

**Constitution of Hydrofluoric Acid and the Fluorides.—** Hydrofluoric acid forms two series of salts corresponding to the two general formulas $MHF_2$ and $M_2F_2$ or MF. The former, of which the salt $KHF_2$ is an example, are called acid fluorides, the latter simply fluorides. The fluorides are commonly represented by the simpler general formula MF, though it appears probable that the doubled formula is more correct. It will be seen later that fluorine forms a large number of so-called double salts or double fluorides, which it is difficult to explain in any other way than that they are derived from the acid $H_2F_2$. Thus cryolite, to which reference has been made, is called a double fluoride of aluminium and sodium, and is generally expressed by the formula $AlF_3 . 3NaF$, which means simply that in some way aluminium fluoride is combined with three molecules of sodium fluoride; but it is difficult to see how this union can be effected without assuming that fluorine has a greater valence than one. If hydrofluoric acid has the

formula $H_2F_2$, its constitution is probably this: H–F–F–H; or possibly H–F=F–H. In the one case the fluorine is represented as bivalent, in the other as trivalent, but we have no evidence in favor of either view as opposed to the other. Still it is generally observed that when the valence of an element varies, it changes from odd to odd or from even to even. Thus in the case of the oxygen acids of chlorine, it appears that the valence of chlorine varies from 1 to 3 to 5 to 7. Similarly the valence of sulphur varies from 2 to 4 to 6, etc. For this reason the view that fluorine is trivalent in hydrofluoric acid is perhaps to be preferred to the simpler view that it is bivalent. If then the constitution of hydrofluoric acid be expressed thus, H–F=F–H, the formation of the so-called double fluorides is not difficult to understand. The double fluoride above referred to, viz., cryolite, has probably the constitution represented by the formula

$$Al\begin{cases} F=F-Na \\ F=F-Na \\ F=F-Na \end{cases}$$, and the other double fluorides are to be

regarded as having a similar constitution.

**Compound of Fluorine with Iodine.**—The only compound of fluorine with the members of the chlorine group is iodine pentafluoride, $IF_5$.* This is a liquid which is formed by treating silver fluoride, AgF, with iodine. Water decomposes it, forming iodic acid:

$$IF_5 + 3H_2O = 5HF + HIO_3.$$

Considering the compounds which the halogens form with one another, it appears that iodine combines with bromine to form the compound IBr, with chlorine it forms $ICl_3$, and with fluorine $IF_5$; or its valence towards bromine is 1, towards chlorine 3, and towards fluorine 5. The farther removed in the series the element is from iodine the greater is the valence of iodine for it.

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* There seems to be some doubt in regard to the existence of this compound.

**Tabular Presentation of the Compounds of the Members of the Chlorine Family with Hydrogen, with Oxygen, with Hydrogen and Oxgen, and with One Another.**

*Compounds with Hydrogen.*

$HF(H_2F_2)$     HCl       HBr       HI

*Compounds with Oxygen.*

| —— | $Cl_2O$ | —— | —— |
| —— | $Cl_2O_3$ | —— | —— |
| —— | $ClO_2$ | —— | —— |
| —— | —— | —— | $I_2O_5$ |

*Compounds with Hydrogen and Oxygen.*

| —— | HClO | HBrO | |
| —— | $HClO_2$ | —— | |
| —— | $HClO_3$ | $HBrO_3$ | $HIO_3$ |
| —— | $HClO_4$ | —— | $HIO_4(H_5IO_6)$ |

*Compounds with One Another.*

ClBr       ICl, IBr
           $ICl_3, IF_5$

**Relative Affinities of the Elements of the Chlorine Group.**—The difference between the affinities of these elements, which has already been commented upon, is illustrated in a number of ways. From iodides, chlorine and bromine set iodine free ; and from bromides, chlorine sets bromine free. When chlorine is added to a solution containing a bromide and an iodide, it first sets the iodine free, and forms the corresponding chloride. Thus, in the case of potassium iodide :

$$2KI + Cl_2 = 2KCl + I_2.$$

After this reaction is complete, the chlorine acts upon the water, decomposing it, oxidizing the iodine to iodic acid (which see). The solution is then colorless. After all the iodine is converted into iodic acid the bromine is liberated and colors the solution yellowish red.

Again, as we shall see, there are some oxidizing agents which decompose iodides but which do not decompose bromides and chlorides, and others which decompose chlorides but do not decompose bromides and iodides.

### Family VII, Group A—Manganese.

There is one element which belongs in the same family as those which have just been treated, and resembles them in some respects; but at the same time it differs from them quite markedly in other respects. This is manganese. It acts in fact in two different ways, and is one of those elements, already referred to, which are both acid-forming and base-forming. Some of its compounds with hydrogen and oxygen are distinctly acid, others are distinctly basic. So far as it acts like the members of the chlorine family a brief reference to it here is desirable. On the other hand, it will be dealt with chiefly in connection with those base-forming elements which it most resembles, as, for example, iron.

Manganese occurs in nature principally in the form of pyrolusite or manganese dioxide, $MnO_2$, also known as the black oxide of manganese. It forms with oxygen compounds of the following formulas: $MnO$, $Mn_2O_3$, $Mn_3O_4$, $MnO_2$, and $Mn_2O_7$. When a compound of manganese is subjected to the influence of powerful oxidizing agents in the presence of an alkali it is converted into a salt of *manganic acid*, $H_2MnO_4$, which in its composition resembles sulphuric acid. If the salt of manganic acid thus obtained is dissolved in water it undergoes partial decomposition, which is complete if the solution is boiled, or if carbon dioxide is passed through it. The change consists in the transformation of manganic acid into *permanganic acid*, $HMnO_4$:

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O \; ; \; \text{or}$$
$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

*Permanganic acid*, $HMnO_4$, is a compound which in many respects resembles perchloric acid. It can be ob-

tained in water solution by decomposition of certain of its salts, but like perchloric acid it is easily decomposed. In consequence of the ease with which it gives up oxygen it is a good oxidizing agent, and is extensively used in the laboratory in this capacity. It is employed in the form of the potassium salt, *potassium permanganate,* $KMnO_4$, which will receive special attention under the head of Manganese Compounds. In order, however, to make clear the difference in conduct between perchloric and permanganic acids a few characteristic facts will be mentioned here. The conduct of permanganic acid and of potassium permanganate will be understood, if it is borne in mind that in the presence of substances of strongly acid character manganese tends to act as a base-forming element, and in this capacity to form salts with the acids. Thus in presence of sulphuric acid potassium permanganate forms potassium sulphate, manganous sulphate, and oxygen, if there is anything present which has the power to take up oxygen. In the salts in which it plays the part of a metal manganese is generally bivalent. With hydrochloric acid, as we have already seen in studying the action of hydrochloric acid upon manganese dioxide, it forms the chloride $MnCl_2$. When now potassium permanganate is treated with hydrochloric acid it is decomposed according to the following equation :

$$2KMnO_4 + 6HCl = 2KCl + 2MnCl_2 + 3H_2O + 5O.$$

Similarly, with sulphuric acid manganous sulphate is formed, thus :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Such reactions do not take place with perchloric acid, as chlorine is entirely lacking in the power to enter into acids in the place of the hydrogen and form salts.

Manganese forms some other acids besides permanganic acid, but they exhibit little or no analogy with compounds of chlorine, and their study will therefore be postponed until manganese is taken up. The point of

chief interest to be noted here is that this element is un-mistakably like chlorine in its highest oxygen com-pounds, but entirely different from it in most of its com-pounds. The compound *manganese heptoxide*, $Mn_2O_7$, stands in the relation of an anhydride to permanganic acid. In water solution it passes over into the acid:

$$Mn_2O_7 + H_2O = 2HMnO_4.$$

It is formed by treating potassium permanganate with the most concentrated sulphuric acid:

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + Mn_2O_7 + H_2O.$$

It is extremely unstable, giving up oxygen readily. In contact with organic substances or other substances which have the power to take up oxygen it decomposes so rapidly as frequently to lead to explosions. It is of interest to note that this is the only oxide of Family VII in which the maximum valence of 7 is shown.

Judging by analogy, it seems probable that the consti-tution of permanganic acid is like that of periodic and perchloric acids, and is represented by the formula

$$O=\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Mn}}}}-O-H,$$ in which the manganese is septivalent.

# CHAPTER XIII.

### THE ELEMENTS OF FAMILY VI, GROUP B:
### SULPHUR—SELENIUM—TELLURIUM.

**Introductory.**—The elements of this group bear to oxygen a relation somewhat similar to that which the elements of Group B, Family VII, bear to fluorine. The three members sulphur, selenium, and tellurium resemble one another fully as strikingly as chlorine, bromine, and iodine do. Their compounds bear a general resemblance to those of oxygen, and yet they form very characteristic compounds with oxygen, while oxygen forms no analogous compounds with any of them. Just as iodine forms a compound with fluorine of the formula $IF_5$, but fluorine does not form with iodine a compound $FI_5$, so sulphur, selenium, and tellurium form with oxygen the compounds $SO_3$, $SeO_3$, and $TeO_3$, while oxygen does not form analogous compounds with these other elements. The valence of the elements of this group towards hydrogen is 2, as shown in the compounds $H_2O$, $H_2S$, $H_2Se$, and $H_2Te$. Of oxygen and sulphur there are other hydrogen compounds, as hydrogen dioxide, $H_2O_2$, and an analogous compound of sulphur, but there is great uncertainty in regard to the constitution of the latter compound, and practically nothing is known in regard to the valence of sulphur in it. In general the hydrogen valence is constant. Towards the members of the chlorine group the valence varies from 2 to 6. Oxygen never exhibits a higher valence than 2 towards chlorine and its analogues. The compound $OCl_2$ illustrates the bivalence of oxygen towards chlorine. Sulphur forms with chlorine the compounds $S_2Cl_2$ and $SCl_2$, which are analogous to the hydrogen compounds $H_2S_2$ and $H_2S$, and in both of them the sulphur is probably bivalent. It also forms the compound $SCl_4$, in which it is quadrivalent. With iodine it

is said to form the unstable compounds $S_2I_2$ and $SI_6$. Selenium and tellurium form similar compounds, and, in general, the stability of the compounds of the members of the sulphur group with the members of the chlorine group increases in the order sulphur, selenium, tellurium. Sexivalence of these elements towards members of the chlorine group is rare, being shown only in the compound $SI_6$, and even this is doubtful.

Towards oxygen the three elements of the sulphur group are quadrivalent and sexivalent, as seen in the compounds $SO_2$, $SeO_2$, $TeO_2$, and $SO_3$, $SeO_3$, and $TeO_3$. Of course, it is possible that in these oxygen compounds the elements are bivalent. Thus, sulphur dioxide, $SO_2$,

may be represented by the formula $S\!\!<^O_O$, in which

both the oxygen and the sulphur appear as bivalent; and, in a similar way, the trioxide may be represented by the

formula $S\!\!<^{O}_{O}\!\!>O$ ; but the only reason for doing this is

the desire to represent sulphur as always bivalent. The existence of the compounds $SCl_4$, $SeCl_4$, and $SI_6$ cannot be explained, however, on the assumption that sulphur is bivalent, and the simplest view which can be taken of the matter is that the members of the sulphur group are in general bivalent towards hydrogen; bivalent, quadrivalent, and, exceptionally, sexivalent towards the members of the chlorine group; and quadrivalent and sexivalent towards oxygen. Towards hydroxyl the valence of the members of the sulphur group appears to vary from 4 to 6. The quadrivalence is shown in the compound hydrosulphurous acid, $H_2SO_2$, which probably has

the constitution $O{=}\overset{\overset{\textstyle H}{|}}{S}{-}O{-}H$ ; the sexivalence is seen in

sulphuric acid, $H_2SO_3$, or $H{-}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}{-}O{-}H$, and in sulphuric

acid, $S(OH)_6$, or in the ordinary form $H_2SO_4$, or

$$H-O-\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O}{\|}}{S}}-O-H.$$

Of the three elements of this group sulphur occurs in greatest abundance in nature, selenium next in order, and finally tellurium. Just as bromine frequently accompanies chlorine, so selenium frequently accompanies sulphur, but it is always present in much smaller quantity than sulphur. Tellurium occurs in very small quantity relatively, and not uncommonly in combination with valuable metals like gold and silver. Large quantities of sulphur are found in the *native* or uncombined condition. Only extremely small quantities of selenium and tellurium are found native.

## SULPHUR, S (At. Wt. 31.83).

**Occurrence.**—The principal deposits of native sulphur are found in Sicily, Italy, and Spain. In California also there is a considerable deposit. In general, sulphur is likely to be found near dying or extinct volcanoes. Sulphur occurs in nature, further, in the form of the hydrogen compound, hydrogen sulphide, $H_2S$, issuing from the earth in volcanic regions, and in solution in some natural waters, known as "sulphur waters." The oxide $SO_2$ is likewise found issuing from the earth in volcanic regions. Compounds of sulphur with metallic elements, as with iron, copper, lead, zinc, are very abundant. Such compounds are iron pyrites, $FeS_2$; copper pyrites, $CuFeS_2$; galenite, $PbS$; and zinc blende, $ZnS$. Some sulphates are widely distributed and occur in large quantities; for example, gypsum or calcium sulphate, $CaSO_4 + 2H_2O$; barium sulphate, or heavy spar, $BaSO_4$; lead sulphate, $PbSO_4$. Finally, sulphur occurs in a few animal and vegetable products in combination with carbon, hydrogen, and, generally, with nitrogen.

**Extraction of Sulphur from its Ores.**—By far the largest quantity of sulphur found in the market is taken from

the mines in Sicily. Of these mines there are between 250 and 300. When taken from the mines it is mixed with many earthy substances, from which it must be separated. The separation is generally effected in Sicily by piling the ore so as to leave passages for air, covering the piles with earthy matter to prevent free access of air and then setting fire to them. A part of the sulphur burns, and this causes the rest of the sulphur to melt. The molten sulphur runs down to the bottom of the pile, and by a proper arrangement it is drawn off from time to time. If the pile of ore were not covered up, and the air were allowed to enter freely, the sulphur would burn up, and be converted into the gas sulphur dioxide. The " crude brimstone " obtained in the manner described is afterwards refined by distillation, and it is this refined or distilled sulphur which is met with in the market under the names " roll brimstone " and " flowers of sulphur."

The distillation is carried on in retorts made of earthenware, and these are connected with large chambers of brick-work. When the vapor of sulphur first comes into the condensing-chamber it is suddenly cooled, and hence deposited in the form of a fine powder. This is what is called " flowers of sulphur." After the distillation has continued for some time the vapor condenses in the form of a liquid, which collects at the bottom of the chamber. This is drawn off into slightly conical wooden moulds, and takes the form of " roll brimstone" or " stick sulphur."

Some sulphur is obtained from iron pyrites by heating in closed vessels. The change which takes place on heating iron pyrites is perfectly analogous to that which takes place on heating manganese dioxide in preparing oxygen. A sulphur compound of the formula $Fe_3S_4$ and free sulphur are formed in the former case, as the compound of manganese and oxygen, $Mn_3O_4$, and free oxygen are formed in the latter :

$$3FeS_2 = Fe_3S_4 + S_2;$$
$$3MnO_2 = Mn_3O_4 + O_2.$$

**Properties.**—Sulphur is a yellow, brittle substance which at − 50° is almost colorless. It melts at 114.5°, forming a thin, straw-colored liquid. When heated to a higher temperature it becomes darker and darker in color, and at 200° to 250° it is so viscid that the vessel in which it is contained may be turned upside down without danger of its running out. Finally, at 448.4° it boils, and is then converted into a brownish-yellow vapor. When molten sulphur solidifies, or when it is deposited from a solution, it takes the form of crystals. But, strange to say, the crystals formed from molten sulphur are entirely different from those deposited from cold solutions of sulphur. The latter belong to the rhombic system. They are octahedrons with a rhombic base. And this is the form of the sulphur found in nature. The former are honey-yellow needles. An examination of these needles shows that the angles which their faces form with one another are not the same as the angles formed by the faces of the octahedrons, and that they belong to an entirely different system—the monoclinic.

The rhombic crystals of sulphur can be made by dissolving "roll brimstone" in carbon disulphide and allowing the solution to stand. When the liquid has sufficiently evaporated, the sulphur will appear in larger or smaller rhombic crystals, according to the conditions. A comparison of the crystals thus obtained with natural crystals will show that the two have identical or very similar forms. The formation of the needles or monoclinic crystals may be shown by melting a considerable quantity, say a pound or two, of roll brimstone in a sand or Hessian crucible, and allowing the liquid mass to cool slowly. When a thin crust has formed on the surface this should be perforated, and the remainder of the liquid sulphur poured off. The crucible will then be found lined with long, dark yellow, lustrous needles which do not look at all like those obtained from the solution in carbon disulphide. If the monoclinic needles are allowed to lie unmolested they gradually undergo change spontaneously. They lose their lustre and become lighter in color; and now, if examined carefully, they

are found to consist of minute crystals like those found in nature. They have changed to the rhombic form. It is evident, therefore, that the arrangement of the particles in the monoclinic crystals of sulphur is not a stable one. The change is accompanied by a considerable evolution of heat.

Substances which crystallize in two distinct forms are called *dimorphous*. We shall see that carbon also crystallizes in two different forms, and that this kind of phenomenon is met with not unfrequently among chemical compounds. The difference between the two varieties of sulphur suggests that observed between the two forms of oxygen. Whether the explanation is the same in the two cases is doubtful. It appears more probable that the difference in the former case is due to different arrangements of the molecules in the crystals, rather than to different arrangements of the atoms in the molecules. The chemical properties of the two varieties are practically identical. This could hardly be the case if the number of atoms in the molecule were different in the two cases.

Besides the two forms mentioned sulphur can also be obtained in the amorphous, or uncrystallized, condition. If molten sulphur is quickly cooled under water it remains for some time soft and dough-like, and while in this condition it is amorphous. If allowed to stand it gradually becomes hard and brittle.

When separated from certain compounds which are in solution in water, the sulphur is in a very finely divided condition, and gives the liquid the appearance of milk. This is seen on adding hydrochloric acid to a solution of sodium thiosulphate, or hyposulphite, as it is generally called. This substance has the formula $Na_2S_2O_3$, and the reactions which take place between it and hydrochloric acid are these:

$$Na_2S_2O_3 + 2HCl = H_2S_2O_3 + 2NaCl ;$$
$$H_2S_2O_3 = SO_2 + H_2O + S.$$

On treating certain varieties of sulphur with carbon disulphide they are found to dissolve completely. This

is true, for example, of the natural crystals and of those made artificially by deposition from a solution in carbon disulphide. On the other hand, sulphur in the form of "flowers of sulphur" is only partly soluble in the liquid. There are therefore two forms of sulphur to be distinguished between, the *soluble* and the *insoluble*. The cause of the difference between these modifications is not known. "Stick sulphur" is mostly soluble, while in the "flowers of sulphur" there is at times a considerable percentage of the insoluble variety. Sulphur is insoluble in water, and slightly soluble in alcohol and ether.

Sulphur is a much less active element chemically than the members of the chlorine group, and also less active than oxygen. Generally speaking, however, it conducts itself like oxygen. It combines directly though not easily with hydrogen, and it combines readily with most metals, forming compounds called *sulphides* which, so far as their composition is concerned, are analogous to the oxides. Thus when heated together with iron, copper, or lead, combination takes place readily with evolution of heat and light. In its chemical conduct it differs markedly from the members of the chlorine group. When heated to a sufficiently high temperature in the air or in oxygen, sulphur forms the compound sulphur dioxide, $SO_2$, and, under certain conditions which will be described farther on, this combines with more oxygen to form the trioxide $SO_3$. Further, it combines with nearly all the acid-forming elements if heated with them to a sufficiently high temperature. It combines with most other elements less readily than oxygen, and it forms less stable compounds. Thus, its compound with hydrogen is decomposed very much more readily into its elements than water is; and the sulphides or its compounds with metals are decomposed when they are heated in oxygen, the oxygen displacing the sulphur, much as chlorine displaces bromine; though there is a difference between the two cases to be found in the fact that sulphur itself unites readily with oxygen, and this facilitates the decomposition of the sulphides by the action of oxygen.

When treated with powerful oxidizing agents sulphur is converted into sulphuric acid. Thus the action of concentrated nitric acid takes place in the main according to the equation

$$2HNO_3 + S = H_2SO_4 + 2NO.$$

The action of sulphur upon the so-called caustic alkalies, sodium and potassium hydroxides, is somewhat like that of chlorine, bromine, and iodine. It will be remembered that with potassium hydroxide chlorine forms potassium chloride and potassium chlorate or hypochlorite, according to the concentration and temperature of the solution. When sulphur acts upon sodium hydroxide the sulphide is formed, but oxygen is thus rendered available and some of it combines with the sulphide, and sulphur also combines with a part of the sulphide. The principal reactions involved are:

$$(1) \quad 2NaOH + S \;= Na_2S + H_2O + O\,;$$
$$(2) \quad Na_2S \;\;+ 4S = Na_2S_5\,;$$
$$(3) \quad Na_2S \;\;+ S \;+ 3O = Na_2S_2O_3.$$

Expressing these reactions in one equation we have

$$6NaOH + 12S = 2Na_2S_5 + Na_2S_2O_3 + 3H_2O.$$

The action is of the same general character as that which takes place in the case of chlorine, but differs from it in the fact that sodium sulphide, $Na_2S$, has the power to take up sulphur, and also to take up sulphur and oxygen.

The specific gravity of the vapor of sulphur varies with the temperature, and is such as to indicate that at temperatures not far above the boiling point the molecule consists of eight atoms, while at the temperature 800° and higher the molecule consists of two atoms. This suggests the question whether the molecule of sulphur in the solid form may not be more complex than the condition represented by the symbol $S_8$. We have no means of answering this question with any certainty at present.

**Uses of Sulphur.**—Enormous quantities of sulphur are used in the manufacture of sulphuric acid, and of gunpowder. It is also used in the manufacture of fire-works of various kinds. Burning sulphur gives sulphur dioxide, which is extensively employed for bleaching wool, silk, straw, etc. When caoutchouc is thoroughly mixed with sulphur or some sulphur compound it becomes vulcanized.

## COMPOUNDS OF SULPHUR WITH HYDROGEN.

The principal compound of sulphur and hydrogen is analogous in composition to water. It is known as hydrogen sulphide or sulphuretted hydrogen, and has the formula $H_2S$. Besides this there is at least one other compound which contains a larger proportion of sulphur, and probably has the composition $H_2S_2$. There are reasons for supposing, further, that still more complex compounds can exist, but owing to their instability it is impossible to isolate them in pure condition and study them.

**Hydrogen Sulphide, Sulphuretted Hydrogen, $H_2S$.**— When hydrogen is passed over highly heated sulphur the two elements combine to form hydrogen sulphide. The action is, however, quite incomplete and is not to be compared with that which takes place when hydrogen and oxygen are heated together. This compound of sulphur and hydrogen occurs in nature in solution in the so-called "sulphur waters," which are met with in many parts of the world. It is formed by heating organic substances which contain sulphur, just as water is formed by heating organic substances which contain oxygen. It is formed, further, by decomposition of organic substances which contain sulphur, as, for example, the albumen of eggs. The odor of rotten eggs is partly due to the formation of hydrogen sulphide. It is formed by the action of acids upon sulphides or hydrosulphides, just as water is formed by the action of acids upon oxides or hydroxides (see p. 132). Thus hydrochloric acid and ferrous sulphide, FeS, give ferrous chloride, $FeCl_2$, and hydrogen sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S\,;$$

just as ferrous oxide, FeO, and hydrochloric acid give ferrous chloride and water :

$$FeO + 2HCl = FeCl_2 + H_2O.$$

So also potassium hydroxide and potassium hydrosulphide act in the same way, as has been pointed out :

$$KSH + HCl = KCl + H_2S\,;$$
$$KOH + HCl = KCl + H_2O.$$

It is generally formed by the action of nascent hydrogen upon sulphur compounds. Thus, it has been shown that the hydrogen from hydriodic acid has the power to reduce sulphuric acid to hydrogen sulphide :

$$H_2SO_4 + 8HI = H_2S + 4H_2O + 8I.$$

In the laboratory, where the gas is extensively used, it is generally prepared from ferrous sulphide, FeS, and dilute sulphuric acid, which are simply brought together at the ordinary temperature in a flask such as is used in making hydrogen. The reaction is like that which takes place between ferrous sulphide and hydrochloric acid. It is represented by this equation :

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

**Properties.**—Hydrogen sulphide is a colorless, transparent gas of the specific gravity 1.178. It has an extremely disagreeable odor, somewhat suggestive of that of rotten eggs. It is poisonous, even small quantities causing headache, vertigo, nausea, and other bad symptoms. It burns with a blue flame, forming water and sulphur dioxide :

$$H_2S + 3O = H_2O + SO_2.$$

If, however, the air has not free access, as when the gas is burned in a cylinder open at one end, only a part of the sulphur is burned, the rest being deposited upon the walls of the vessel, while the hydrogen burns. The gas is soluble in water, about three volumes being taken

up at ordinary temperatures. This solution is used to some extent in the laboratory instead of the gas, but, owing to the fact that it readily undergoes change in consequence of the action of the oxygen of the air, it is not as valuable as it would be if it were more stable. The change consists simply in the oxidation of the hydrogen and the separation of the sulphur. If a bottle containing a solution of hydrogen sulphide is allowed to stand for a few days, particularly if it is opened from time to time, the odor of the gas will disappear and a deposit of sulphur will be noticed in the bottle. The liquid is then nothing but water. When the solution is boiled it loses all the gas contained in it.

Hydrogen sulphide is easily decomposed into its elements. It requires a temperature of only a little above 400° to effect direct decomposition. In consequence of this instability it causes a number of changes which the analogous compound water cannot effect. The relations here are similar to those which exist between hydrochloric and hydriodic acids. Hydrochloric acid is very stable, while hydriodic acid breaks down readily into hydrogen and iodine. Therefore hydriodic acid, as we have seen, acts as a reducing agent, while hydrochloric acid does not. So, also, hydrogen sulphide acts as a reducing agent. Thus, if it be passed into concentrated sulphuric acid this reaction takes place :

$$H_2SO_4 + H_2S = 2H_2O + S + SO_2.$$

The action is to be traced to the decomposition of the hydrogen sulphide into hydrogen and free sulphur, the hydrogen then acting upon the sulphuric acid thus :

$$H_2SO_4 + 2H = 2H_2O + SO_2.$$

With hydriodic acid the reduction may go farther, as has been seen; with hydrobromic acid, however, the action takes place practically in the same way as with hydrogen sulphide.

Chlorine, bromine, and iodine act upon hydrogen

sulphide, setting the sulphur free and uniting with the hydrogen :

$$H_2S + Cl_2 = 2HCl + S.$$

This reaction suggests the decomposition of water by chlorine, but what a difference there is between the two cases! Chlorine decomposes water very slowly and only under the influence of the direct sunlight, while it decomposes hydrogen sulphide completely and instantly. Similarly, hydrogen sulphide has the power to abstract chlorine from some of its compounds, as, for example, from ferric chloride, $FeCl_3$. When this is treated with nascent hydrogen from any source, it is *reduced* to ferrous chloride, $FeCl_2$, thus :

$$FeCl_3 + H = FeCl_2 + HCl.$$

So, also, when it is treated with hydrogen sulphide it is reduced in the same way in consequence of the action of the hydrogen :

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

The instability of hydrogen sulphide is further shown by the ease with which it is decomposed by metals with liberation of hydrogen and formation of sulphides. It will be remembered that at high temperatures several metals decompose water, but that at ordinary temperatures only a few decompose it easily. Hydrogen sulphide acts much more readily ; a number of metals which do not act upon water even at high temperatures, as silver, gold, and mercury, decompose this gas at ordinary temperatures.

Hydrogen sulphide acts upon metallic oxides, converting them into sulphides, as for example :

$$CuO + H_2S = CuS + H_2O.$$

**Action of Hydrogen Sulphide upon Solutions of Salts— Use in Chemical Analysis.**—Hydrogen sulphide is extensively used in every chemical laboratory as a reagent in chemical analysis. In order that its action may be understood a few words of explanation are necessary. Sulphur, as we have seen, has a strong affinity for the

metallic or base-forming elements, forming with them the sulphides. Further, hydrogen sulphide is easily decomposed, and the substitution of metals for the hydrogen is facilitated by this fact. If now a salt is in solution in water and hydrogen sulphide is passed into the solution there will, of course, be the tendency to the formation of the sulphide of the metal contained in the salt. Thus, suppose the salt in solution is silver nitrate, $AgNO_3$. On passing hydrogen sulphide into this solution the silver will tend to combine with the sulphur to form the sulphide, $Ag_2S$. If this is formed, hydrogen must be freed from the hydrogen sulphide, and this would probably take the place of the silver in the nitrate, forming nitric acid, according to this equation:

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3.$$

If the dilute acid thus formed has the power to decompose silver sulphide the sulphide will not be formed; but if it has not this power the sulphide will be formed, and it will be thrown down or precipitated if it is an insoluble compound. The sulphides of some metals are not decomposed by dilute acids, and are insoluble in water. If hydrogen sulphide is passed through solutions of the salts of these metals the sulphides are thrown down.

Secondly, the sulphides of some metals are decomposed by dilute acids. Plainly, these cannot be thrown down by simply passing hydrogen sulphide through the solutions of their salts, whether they are soluble or insoluble in water. Thus, for example, the sulphide of iron, FeS, is insoluble in water, but it is easily decomposed by dilute acids, and therefore when hydrogen sulphide is passed through a solution of an iron salt the sulphide is not precipitated. In the case of the sulphate the reaction would be

$$FeSO_4 + H_2S = FeS + H_2SO_4.$$

But the dilute sulphuric acid would decompose the sulphide, and the reaction does not take place. If, however, a soluble sulphide is added to a solution of such a metal,

decomposition takes place. Thus, if, instead of passing hydrogen sulphide, a solution of potassium sulphide is added, reaction takes place thus:

$$FeSO_4 + K_2S = K_2SO_4 + FeS.$$

Here no sulphuric acid is formed, but, instead of it, neutral potassium sulphate, which does not act upon the insoluble sulphide. Advantage is taken of this fact in chemical analysis, but, in place of potassium sulphide, the analogous compound, ammonium sulphide, $(NH_4)_2S$, is used. This acts in the same way. Thus, in the case above cited the action with ammonium sulphide is represented by this equation:

$$FeSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + FeS.$$

There are several metals which act towards hydrogen sulphide in the same way that iron does.

Thirdly, there are some metals whose sulphides are soluble in water, and, therefore, if solutions of their salts are treated with hydrogen sulphide or with ammonium sulphide no apparent action takes place.

Facts like those just referred to form a good basis for the division of the metallic elements into groups for purposes of analysis. According to the above these elements can be divided into three great groups, as follows:

I. Metals whose sulphides are insoluble in water and not decomposed by dilute acids. This is called *the hydrogen sulphide group*. It includes lead, bismuth, silver, mercury, copper, cadmium, gold, platinum, tin, antimony, and arsenic.

II. Metals whose sulphides are insoluble in water but are decomposed by dilute acids. They are therefore not precipitated by hydrogen sulphide, but are precipitated by soluble sulphides. As ammonium sulphide is used for the purpose of effecting the precipitation the group is known as *the ammonium sulphide group*. It includes iron, nickel, cobalt, manganese, thallium, zinc, and uranium. Further, the two elements aluminium and chromium are thrown down with the above, not as sul-

phides but as hydroxides, and they are therefore included in the group.

III. Metals whose sulphides are soluble in water. This group includes all the metals not included in the above two.

By taking advantage, then, of the properties of the sulphides of the metals they can be divided into these three groups, and the detection of any particular element is thus facilitated. If hydrogen sulphide is passed through a solution, and a precipitate formed, we know that this can contain only those metals which belong to the hydrogen sulphide group; and so on. Now, if the precipitate formed with hydrogen sulphide is treated with certain other reagents other changes take place, and by further study it is quite possible, and indeed comparatively simple, to determine which of the members of the group are present.

One reaction made use of in further examination of the hydrogen sulphide precipitate is particularly interesting in this connection. Under the head of Acids and Bases compounds were referred to which were called sulphur acids and sulphur bases. Corresponding to the oxygen acid known as arsenic acid, which has the formula $H_3AsO_4$, there are salts which are plainly derived from the corresponding sulphur acid $H_3AsS_4$. Such salts are formed by treating arsenic sulphide with soluble sulphides, as for example ammonium sulphide :

$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

So, too, tin forms an oxygen acid, $H_2SnO_3$; and salts of the corresponding sulphur acid, $H_2SnS_3$, are formed by treating the sulphide of tin with soluble sulphides :

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

Now some of these sulphur salts are soluble in water. This is true of the ammonium salts. So that when the sulphides of metals which have the power to form salts of this kind are treated with ammonium sulphide they pass into solution. Of the metals of the

hydrogen sulphide group only arsenic, antimony, and tin have this power; so that, if the hydrogen sulphide precipitate is treated with ammonium sulphide, arsenic, antimony, and tin sulphides are dissolved if present, whereas the other sulphides are not changed by this treatment. Thus a means is afforded of subdividing the hydrogen sulphide group into two sub-groups: (*a*) Metals whose sulphides are insoluble in ammonium sulphide; and (*b*) metals whose sulphides are soluble in ammonium sulphide.

**Hydrosulphides.**—The action of hydrogen sulphide shows that it belongs to the class of acids. When it acts upon an oxide the corresponding sulphide and water are formed. But just as there are sulphides which are derived from hydrogen sulphide by the replacement of both hydrogen atoms by metallic elements, so there are hydrosulphides which are derived from it by the replacement of only one of the two atoms of hydrogen in the molecule. The sulphides correspond to the oxides, and the hydrosulphides to the hydroxides. Thus the analogous oxygen and sulphur compounds of potassium are :

$$K_2O \qquad K_2S$$
$$KOH \qquad KSH.$$

We speak of sulphides and hydrosulphides as salts of hydrogen sulphide. In consequence of this ability to form salts in the same way in general that acids do, hydrogen sulphide is sometimes called *sulphydric acid*, and the salts of the formula $MSH$, *sulphydrates*. The name sulphydrate is analogous to hydrate, which, as has been pointed out, is used by some to designate the compounds of the formula $MOH$ or the hydroxides. Between the acid, hydrogen sulphide, and the neutral compound, water, there is no fundamental difference. The difference is simply one of degree. In the present system of chemistry, which is largely an oxygen system, water is regarded as the connecting link between acids and bases, as was shown on p. 135. But we might with equal right base our defi-

nitions and conceptions of acids and bases upon the conduct of sulphur compounds, and thus build up a sulphur system. In such a system hydrogen sulphide would be the connecting link between acids and bases.

**Hydrogen Persulphide, $H_2S_2(?)$.**—The sulphides of certain metals, particularly the so-called alkali metals, sodium and potassium, combine with sulphur to form the polysulphides, examples of which are $K_2S_2$, $K_2S_3$, $K_2S_4$, and $K_2S_5$. When these are decomposed with dilute acids compounds of hydrogen and sulphur are formed. It has thus far, however, been impossible to determine whether more than one such compound is formed, for the reason that there is no means of deciding whether the substances formed are chemical compounds or mere mixtures of sulphur and some one compound of sulphur and hydrogen. Hydrogen persulphide is a liquid with a very disagreeable odor. Just as hydrogen dioxide decomposes readily into water and oxygen, so hydrogen persulphide decomposes readily into hydrogen sulphide and sulphur.

Concerning the constitution of hydrogen persulphide nothing definite is known. If the constitution of hydrogen dioxide is H–O–O–H, and hydrogen persulphide is a disulphide, it seems probable that it has the constitution H–S–S–H, but there is no evidence bearing upon this point. The fact that the sulphides can take up four and only four atoms of sulphur, just as they can take up four and only four atoms of oxygen, taken together with the general similarity between the conduct of oxygen and that of sulphur, suggests that these two reactions may be of the same kind:

$$K_2S + 4S = K_2SS_4 ;$$
$$K_2S + 4O = K_2SO_4.$$

But for reasons which will be more fully presented under Sulphuric Acid (which see), it is generally believed that in this acid two of the oxygen atoms are in direct combination with sulphur alone, while two are in combination with sulphur and hydrogen. If the polysul-

phide has a similar constitution it must be represented

by the formula $K-S-\overset{\overset{S}{\|}}{S}-S-K$, and, further, if the structure

$\underset{\underset{S}{\|}}{}$

of the polysulphide be as here represented, it is possible that persulphide of hydrogen has a similar constitution.

**Compounds of Sulphur with Members of the Chlorine Group.**—Sulphur combines directly with chlorine and forms the compounds $S_2Cl_2$, $SCl_2$, and $SCl_4$. Of these the first is the most stable. This can be boiled without undergoing decomposition. The second, sulphur dichloride, $SCl_2$, undergoes decomposition into chlorine and sulphur monochloride at the boiling point; while sulphur tetrachloride exists only at low temperatures. All these compounds are decomposed by water, yielding oxygen compounds. In referring to the differences between the acid-forming and the base-forming elements, attention was called (see p. 125) to the fact that, in general, the oxides of the base-forming elements are decomposed by hydrochloric acid, yielding metallic chlorides and water; whereas with the acid-forming elements the reverse is true, that is to say, the chlorides of the acid-forming elements are, in general, decomposed by water yielding oxides or hydroxides and hydrochloric acid. The truth of this general statement is illustrated by the compounds of sulphur and chlorine. But the products formed, except in the case of the tetrachloride, are not strictly analogous to the chlorides which are decomposed. Thus, if in the monochloride $S_2Cl_2$ oxygen were simply substituted for chlorine, the product would be $S_2O$; but there is no compound of oxygen of this composition, the simplest one being sulphur dioxide, $SO_2$, and this is formed. The excess of sulphur set free, above that required for the formation of the dioxide, is precipitated. The main part of the reaction is represented thus:

$$2S_2Cl_2 + 2H_2O = 4HCl + SO_2 + 3S.$$

The decomposition of the other chlorides takes place in

a similar way. That of the dichloride is represented by the equation

$$2SCl_2 + 2H_2O = SO_2 + 4HCl + S.$$

That of the tetrachloride consists simply in the direct replacement of the chlorine by oxygen.

Of the other compounds of sulphur with members of the chlorine group, the hexiodide, $SI_6$, is perhaps the most interesting, as it shows that sulphur can be sexivalent towards other elements than oxygen. This hexiodide is an extremely unstable compound. There is doubt as to its existence.

## SELENIUM, Se (At. Wt. 78.42).

**Occurrence.**—Selenium occurs only in small quantity in nature. It was first found in the deposit formed in a sulphuric acid chamber (see p. 215), and owed its origin to the presence of small quantities of selenides in the sulphides used in the operation. It was found to resemble tellurium, and for that reason was called selenium, from σελήνη, the moon, tellurium receiving its name from *tellus*, the earth. Selenium occurs in a number of the natural sulphides, such as iron pyrites, copper pyrites, zinc blende, etc.; and when these are treated in a current of air to decompose them and convert the sulphur into sulphur dioxide, the selenium is also oxidized, and the selenium dioxide thus formed is carried into the flues and other parts of the apparatus. As it is a solid it is easily condensed, and gradually a considerable quantity collects in the flues. This flue-dust is the best material from which to make selenium. For the purpose of extraction the dust is treated with oxidizing agents, and the selenium converted either into selenious acid, $H_2SeO_3$, or a salt of selenic acid, $H_2SeO_4$. This is then reduced by proper means. Thus selenious acid is reduced to selenium by passing sulphur dioxide through its solution:

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4.$$

Hydrogen sulphide also reduces selenious acid, forming, however, not free selenium, but selenium sulphide, $SeS_2$, analogous to sulphur dioxide and selenium dioxide:

$$H_2SeO_3 + 2H_2S = 3H_2O + SeS_2.$$

**Properties.**—There are two modifications of selenium, corresponding to those of sulphur. One is soluble in carbon disulphide, the other is not. The soluble form is obtained by reducing selenious acid by means of sulphurous acid, or by means of other reducing agents. The insoluble variety is obtained by melting selenium, then cooling it down suddenly to 210°, and keeping it at this temperature for some time. When it solidifies it is found to be no longer soluble in carbon disulphide. Selenium burns as sulphur does, forming the oxide $SeO_2$, which has the odor of rotten horse-radishes.

**Hydrogen Selenide, $H_2Se$.**—This compound is made in the same way as the corresponding compound of sulphur, by treating a selenide, as, for example, ferrous selenide, FeSe, with an acid. It is a gas, which is soluble in water, and has an odor something like that of hydrogen sulphide, but it produces much more powerful effects upon the olfactory nerves, temporarily destroying the sense of smell and causing painful sensations.

The compounds of selenium with the members of the chlorine group present no features of special interest or importance. In general they resemble the corresponding compounds of sulphur, but are more stable. No iodide of selenium corresponding to the hexiodide of sulphur has been discovered.

## TELLURIUM, (Te At. Wt. 126.52).

**Occurrence.**—Tellurium occurs in some gold ores in the native or uncombined condition, and also in combination with gold, silver, antimony, lead, and other metals. Tellurides occur, among other places in the United States, in California and Virginia. The general method of preparing tellurium from its ores is the same as that by which selenium is made. The tellurium is

oxidized to tellurious acid, $H_2TeO_3$, which is isolated, and then reduced by means of sulphurous acid.

**Properties.**—Tellurium is silver-white, and crystallizes easily. Heated in the air it burns, forming a thick white cloud of tellurium dioxide, $TeO_2$. Treated with sulphuric acid it is oxidized to tellurious acid, $H_2TeO_3$, the sulphuric acid being reduced. Nitric acid oxidizes it likewise to tellurious acid. Melted together with potassium nitrate it is converted into potassium tellurate, $K_2TeO_4$.

**Hydrogen Telluride, $H_2Te$.**—This compound is made by treating zinc telluride, $ZnTe$, with an acid. It is a gas, which resembles hydrogen sulphide in most of its properties.

Like sulphur and selenium, tellurium combines with the members of the chlorine group. The compounds are more stable than those of the other two elements of the group. Thus, taking the three tetrachlorides, that of sulphur is extremely unstable, being capable of existence only at low temperatures ; that of selenium is more stable, but still it is decomposed when heated to the boiling temperature ; while that of tellurium can be heated far above the temperature of boiling without decomposition.

When tellurium tetrabromide is treated with potassium chloride a compound of the formula $K_2TeBr_6$ is formed, which in composition, as will be observed, is analogous to potassium tellurite, $K_2TeO_3$, two atoms of bromine taking the place of each atom of oxygen. This appears to be a derivative of the acid $H_2TeBr_6$, which is similar in composition to the chlorplatinic acid, $H_2PtCl_6$, referred to on p. 142, and to fluosilicic acid, $H_2SiF_6$. As has already been remarked, not many such compounds of the acid-forming elements are commonly met with, largely for the reason that they are for the most part easily decomposed by water and converted into the corresponding oxygen compounds.

# CHAPTER XIV.

## COMPOUNDS OF SULPHUR, SELENIUM, AND TELLURIUM WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

**Introductory.**—It has already been stated that, when the three elements of the sulphur group are burned in the air, they are converted into the corresponding dioxides. Under certain conditions it is possible to convert sulphur dioxide and tellurium dioxide into the trioxides $SO_3$ and $TeO_3$, while the corresponding compound of selenium has not been made. A lower oxide of sulphur, $S_2O_3$, and a higher one of the formula $S_2O_7$ have also been made. The dioxides dissolve in water, and from these solutions salts of the general formula $M_2SO_3$, $M_2SeO_3$, and $M_2TeO_3$ are obtained. The trioxide of sulphur dissolves in water with great evolution of heat, forming compounds $S(OH)_6$, $OS(OH)_4$, and $O_2S(OH)_2$.

Most of the salts obtained from this solution are derived from an acid of the formula $H_2SO_4$, and therefore this is generally called sulphuric acid. By treating sulphuric acid with reducing agents of various kinds it can be converted successively into other acids containing a smaller proportion of oxygen; and if the reduction is pushed far enough sulphur and hydrogen sulphide are obtained. The limit of reduction is reached in hydrogen sulphide; and, on the other hand, if hydrogen sulphide is oxidized the limit of oxidation is reached in sulphuric acid. The intermediate products which have been isolated are represented in the following table, by the side of which for the sake of comparison is placed the similar series of chlorine acids :

| | |
|---|---|
| $H_2S$ | $HCl$ |
| —— | $HClO$ |
| $H_2S_2O_4$ | $HClO_2$ |
| $H_2SO_3$ | $HClO_3$ |
| $H_4SO_4$ | $HClO_4$ |

In the chlorine series, however, one member more is known than in the sulphur series. A remarkable fact which has not yet been explained is that in each of the ordinary forms of the acids, both in the chlorine series and in the sulphur series, the number of hydrogen atoms is the same as in the hydrogen compound. Throughout the chlorine series there is but one hydrogen atom in the molecule; throughout the sulphur series there are two. This refers only to those forms of the acid from which most of the salts are derived, and plainly not to such compounds as $OS(OH)_4$ and $S(OH)_6$, which, as we shall see, are closely related to sulphuric acid, just as $OCl(OH)_5$ or $H_5ClO_6$ is closely related to perchloric acid. The number of compounds of sulphur is increased by the power the element possesses of uniting with itself, much as it does with oxygen. Thus the sulphides take up sulphur and are converted into polysulphides, and the limit of action of this kind is a compound of the general formula $M_2SS_4$. This series is complete, the members having the composition represented in the following table:

| | |
|---|---|
| $M_2S$ | $M_2S$ |
| $M_2SS$ | —— |
| $M_2SS_2$ | —— |
| $M_2SS_3$ | $M_2SO_3$ |
| $M_2SS_4$ | $M_2SO_4$. |

Comparing this with the series of oxygen compounds an analogy is apparent, though the second and third members of the oxygen series are lacking. The limit is reached in a compound of the same order in both series.

Again, sulphur can take the place of part of the oxygen in the oxygen acids. Thus compounds of the composition represented by the following formulas are conceivable:

$$H_2SOS \quad \text{or} \quad H_2S_2O \,;$$
$$H_2SO_2S \quad \text{or} \quad H_2S_2O_2 \,;$$
$$H_2SOS_2 \quad \text{or} \quad H_2S_3O \,;$$
$$H_2SO_3S \quad \text{or} \quad H_2S_2O_3 \,;$$
$$H_2SO_2S_2 \quad \text{or} \quad H_2S_3O_2 \,;$$
$$H_2SOS_3 \quad \text{or} \quad H_2S_4O.$$

Of these compounds only that one which has the composition $H_2S_2O_3$ is known. This is thiosulphuric acid or, as it is sometimes called, hyposulphurous acid.

Other complications are occasioned by the combination of sulphur with sulphur in some of the oxygen acids above mentioned. In this way probably is formed the series represented in the following table:

| | |
|---|---|
| Dithionic acid, . . . . . . . . | $H_2S_2O_6$ |
| Trithionic " . . . . . . . . | $H_2S_3O_6$ |
| Tetrathionic " . . . . . . . . | $H_2S_4O_6$ |
| Pentathionic " . . . . . . . . | $H_2S_5O_6$. |

While the number of compounds which sulphur forms with hydrogen and oxygen is comparatively large, the relations between them can be traced without serious difficulty, and, studied in the right way, they are seen to follow certain laws which govern their composition. These relations will be discussed after the main facts concerning the principal compounds have been studied.

The number of compounds which selenium and tellurium form with hydrogen and oxygen is much smaller than in the case of sulphur. The only ones known are those which are analogous in composition to sulphurous acid, $H_2SO_3$, and sulphuric acid, $H_2SO_4$; besides these, however, there are a few compounds known which contain hydrogen, sulphur, selenium, and oxygen. These are closely related to some of the compounds of sulphur with hydrogen and oxygen, being derived from them by the introduction of selenium for a part of the oxygen.

Sulphur combines with oxygen and members of the chlorine group, and also with these elements and hydrogen. The simplest compound of this kind is that which has the composition $SOCl_2$. This is plainly analogous to sulphur dioxide, from which it can be made by substituting two atoms of chlorine for one atom of oxygen in the molecule. While this compound cannot unite directly with more chlorine, a compound of the composition $SO_2Cl_2$ can be made. This is in accordance with what we should expect from a consideration of the conduct of sulphur towards oxygen and towards chlorine respec-

tively. With oxygen it forms a stable compound, $SO_3$, while the limit of combination with chlorine is reached in the compound $SCl_4$, and even this is very unstable. As we commonly say, sulphur is sexivalent towards oxygen and quadrivalent towards chlorine. Towards both together it is also sexivalent, as shown in the compound $SO_2Cl_2$, though the compound $SOCl_4$ does not exist. Just as the simple compounds of sulphur and chlorine are decomposed readily by water, forming oxygen compounds, so these mixed compounds containing oxygen and chlorine are also readily decomposed by water. The decomposition appears to take place as represented in the following equations:

$$SO{<}_{Cl}^{Cl} + {HOH \atop HOH} = SO{<}_{OH}^{OH} + 2HCl;$$

$$SO_2{<}_{Cl}^{Cl} + {HOH \atop HOH} = SO_2{<}_{OH}^{OH} + 2HCl.$$

In the first case, the product formed breaks down into sulphur dioxide and water, so that the main action is represented thus:

$$SO{<}_{Cl}^{Cl} + H_2O = SO_2 + 2HCl,$$

and the change therefore consists in substituting one atom of oxygen for the two atoms of chlorine. It is analogous to the transformation of sulphur tetrachloride into sulphur dioxide:

$$SCl_4 + 2H_2O = SO_2 + 4HCl.$$

As these mixed chlorides and oxides are readily converted into the corresponding acids by treatment with water, they are frequently spoken of as the *chlorides of the acids*, or the *acid chlorides*. Between them and the *anhydrides*, or *acidic oxides*, there is plainly an analogy.

**Sulphuric Acid, $H_2SO_4$.**—The many salts of sulphuric acid can be best explained on the assumption that the forms of sulphuric acid are derived from a compound $S(OH)_6$, just as the salts of periodic acid can be best explained on the assumption of a fundamental compound, $I(OH)_7$. As the latter is called *normal periodic acid*, so

the former is called *normal sulphuric acid.* From normal sulphuric acid by successive losses of water are formed the compounds $H_4SO_5$, $H_2SO_4$, and $SO_3$:

$$S(OH)_6 = OS(OH)_4 + H_2O;$$
$$OS(OH)_4 = O_2S(OH)_2 + H_2O;$$
$$O_2S(OH)_2 = O_3S + H_2O.$$

While these compounds are all known, the salts of sulphuric acid are for the most part derived from the acid containing two hydrogen atoms, viz., $O_2S(OH)_2$. In some salts two of the hydrogen atoms in normal sulphuric acid are replaced by metals, the others remaining. Salts of the general formula $S(OH)_4(OM)_2$ are thus formed. These are generally represented as containing two molecules of water of crystallization, thus: $M_2SO_4 + 2H_2O$. To decide between the two views is at present impossible. In the first place, the question as to the nature of water of crystallization must be answered before it can be said whether there is any conflict between the two views. As far as the assumption of normal sulphuric acid is concerned, it can only be said that similar assumptions in the case of iodine and in that of phosphorus seem to be well founded, and, although it would be difficult to furnish proof positive of the reality of the relations, the above suggestion is by far the simplest which has been made, and it is of great assistance in dealing with the acid derivatives of the elements of Families VII, VI, V, and IV.

For the science as well as for the art of chemistry sulphuric acid is of fundamental importance. It is used daily in every chemical laboratory and in every chemical factory, and in some of the most important branches of chemical industry enormous quantities of it are used. In consequence of the large demand for the acid the process used in preparing it has been studied with great care, and it has reached a high state of perfection. As it furnishes an excellent example of the applications of the facts of science to the building up of an industry, it will be studied with some degree of fulness.

Sulphuric acid has been known for a long time. It was made in the eighteenth century by heating calcined iron vitriol (ferrous sulphate, $FeSO_4$) with sand, and was hence called *oil of vitriol*, a name which still survives. It was also prepared by treating sulphur with saltpeter (potassium nitrate, $KNO_3$). The acid was first prepared on the large scale in England with the use of comparatively large chambers lined with lead. It was known as English sulphuric acid, and is still called by this name.

Sulphuric acid occurs in nature in the form of salts or sulphates, such as calcium sulphate or gypsum, barium sulphate or heavy spar, and others. Although these salts occur in large quantity, the acid is not obtained from them, as there is no economical way of substituting hydrogen for the metal. The preparation of the acid by the substitution of hydrogen for the calcium in calcium sulphate, $CaSO_4$, suggests itself, but this cannot be easily effected by any substance available in quantity. Hydrochloric and nitric acids are made from their salts which occur in nature, the former, as we have seen, from sodium chloride, $NaCl$, the latter from saltpeter or potassium nitrate, $KNO_3$, by treating with sulphuric acid. There is, however, no acid which acts upon the sulphates as sulphuric acid acts upon chlorides, nitrates, and many other salts.

The manufacture of sulphuric acid is based upon the two fundamental facts that (1) when sulphur is burned it is converted into sulphur dioxide, $SO_2$; and (2) when sulphur dioxide is treated with an oxidizing agent in the presence of water it is converted into sulphuric acid:

$$SO_2 \quad + H_2O + O = H_2SO_4; \text{ or}$$
$$SO_2 \quad + H_2O \qquad = H_2SO_3; \text{ and}$$
$$H_2SO_3 + O \qquad \quad = H_2SO_4.$$

The chief difficulty is, of course, experienced in effecting the oxidation of the sulphurous acid. It is accomplished by introducing the gas, sulphur dioxide, into large chambers together with compounds of nitrogen

and oxygen, and steam. That which plays the chief part in effecting the transformation is a mixture of the two oxides NO and $NO_2$. This acts like the trioxide, $N_2O_3$, and it may be represented by this formula. Instead of starting with the trioxide, nitric acid is used in the manufacture of sulphuric acid. This at first reacts with sulphur dioxide and steam, as represented in the equation

$$2HNO_3 + 2SO_2 + H_2O = 2H_2SO_4 + N_2O_3.$$

After this the main reactions are (1) the formation of a compound of the formula $SO_2{<}{NO_2 \atop OH}$, called *nitrosyl-sul-phuric acid;* and (2) the decomposition of the nitrosyl-sulphuric acid by water. These reactions are represented in the two equations following:
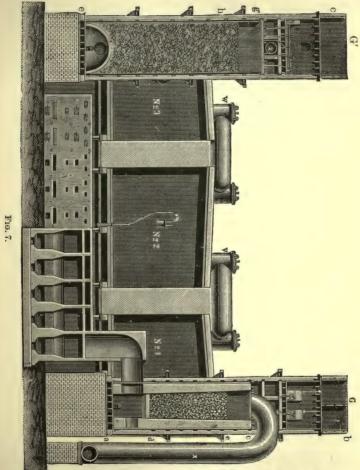
$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(NO_2);$$

$$2SO_2{<}{NO_2 \atop OH} + H_2O = 2SO_2{<}{OH \atop OH} + N_2O_3.$$

The nitrogen trioxide formed in the second reaction then again enters into combination with sulphur dioxide, oxygen, and water to form nitrosyl-sulphuric acid, which again undergoes decomposition with water. It will be seen, therefore, that the trioxide is not lost, but that it simply serves the purpose of effecting the oxidation of the sulphur dioxide, and, theoretically, a small quantity of the gas should be capable of transforming an infinite quantity of sulphur dioxide into sulphuric acid.

Other reactions besides those mentioned above are undoubtedly involved in the manufacture of sulphuric acid, but, according to the most elaborate researches made on the subject in a factory in operation, those mentioned are the principal ones. Whatever the details may be, the oxidation is effected without difficulty, and the waste in nitrogen compounds is now but slight.

The reactions, as has been said, are carried on in large chambers lined with lead, and known as the leaden chambers. The sulphur is burned in a special furnace

so arranged that air has free access to it.  The dioxide
thus formed is then conducted through a tower so con-
structed that it presents a large surface to the action of
the gas.  Through this tower dilute sulphuric acid, taken
from another tower at the end of the system, flows from



Fig. 7.

above, and the hot gases coming in contact with this
serve the purpose of concentrating it, while the gas itself
is cooled before entering the leaden chamber.    The
general arrangement of the essential parts of a sulphuric
acid factory are shown in Fig. 7.

The sulphur dioxide passes through the large tube $x$ into the tower $G$, called the Glover tower. This is filled from $d$ to $e$ with pieces of fire-brick over which from the cistern $b$ a continual stream of dilute sulphuric acid flows. The gases are thus cooled down and the acid concentrated. From a second cistern there flows at the same time concentrated sulphuric acid from the tower $G'$, or the Gay Lussac tower. This stronger acid contains oxides of nitrogen in combination, and by contact with the dilute acid the oxides are set free and are thus mixed with the sulphur dioxide. The nitric acid is introduced into the first chamber, No. 1, in the form of vapor, together with the oxides of nitrogen and sulphur dioxide, and here also the gases meet with water vapor. The reactions above referred to now take place. From the first chamber the gases pass through the pipe $v$ into the second, from this into the third at $w$, and finally, in order to prevent the escape of any unused oxides of nitrogen, the gases are passed through the Gay Lussac tower $G'$. This contains coke over which is kept flowing concentrated sulphuric acid which takes up the oxides of nitrogen and will give them up again when diluted. This liberation of the oxides of nitrogen is accomplished, as has been said, in the Glover tower. The concentrated acid collected at the bottom of the Glover tower is well adapted for use in the Gay Lussac tower. The leaden chambers in some factories are nearly 100 feet long, 18 to 30 feet broad, and 15 feet high.

The acid taken from the chambers contains about 64 per cent of the compound $H_2SO_4$, and has the specific gravity 1.5. This is evaporated first in lead pans until it reaches the specific gravity 1.75. As stronger acid acts upon lead, the evaporation beyond this point is carried on in platinum, glass, or iron. The strong acid thus obtained, which has a specific gravity of about 1.830, is the concentrated sulphuric acid of commerce.

Instead of sulphur, iron pyrites is now extensively used for the preparation of sulphur dioxide in the manufacture of sulphuric acid. This is a compound of iron

and sulphur of the composition $FeS_2$. When it is heated in contact with the air it is converted into the oxide, and the sulphur passes off in the form of sulphur dioxide. If the sulphide used contains selenides the selenium dioxide formed in the roasting process is carried into the flues, and is there deposited with the flue-dust, as was stated in speaking of the source of selenium.

Commercial sulphuric acid is an oily liquid, usually somewhat colored by impurities. The nature of the impurities is dependent upon the substances used in the manufacture and upon the conditions. It often contains some lead sulphate in solution, and when it is diluted with water this separates, giving the liquid a more or less cloudy appearance. By standing, however, the liquid becomes clear, as the lead sulphate collects at the bottom. For obvious reasons, some oxides of nitrogen are also generally present. Among other impurities frequently met with in the commercial acid are arsenic from the pyrites, and a little selenium.

**Pure Sulphuric Acid** is made from the commercial acid by treating it with such substances as will remove the oxides of nitrogen and arsenic, and by distilling. It is a colorless liquid at the ordinary temperature. The pure acid generally made has about the same concentration as the commercial crude acid. By taking special precautions in the distillation a product having very nearly the composition $H_2SO_4$ can be obtained. This is a thick, clear liquid of specific gravity 1.854 at 0°. When cooled down to a low temperature it forms large crystals which melt at 10°.5. When heated it gives off some sulphur trioxide in consequence of partial decomposition into this substance and water:

$$H_2SO_4 = H_2O + SO_3.$$

It finally boils, however, at the temperature 338°, and the distillate has the composition represented by the formula $H_2SO_4 + \frac{1}{12}H_2O$. Heated somewhat above its boiling point it is completely decomposed into sulphur trioxide and water, according to the above equation. If the heating is carried to a higher temperature the sul-

phur trioxide breaks down into sulphur dioxide and oxygen.

Sulphuric acid has a strong tendency to absorb water, and to form compounds with it. In consequence of the formation of these compounds a great deal of heat is evolved when sulphuric acid is mixed with water. One molecule of sulphuric acid when mixed with about 1600 molecules of water gives 17,850 cal. Among the compounds thus formed are the so-called hydrates of the composition $H_2SO_4 + H_2O$, and $H_2SO_4 + 2H_2O$, which should probably be regarded as having the constitution $OS(OH)_4$ and $S(OH)_6$.

So strong is the tendency of the acid to combine with the elements of water that it abstracts them in the proportions to form water from many organic substances. Thus a piece of wood placed in sulphuric acid soon turns black and is completely disintegrated. The cause of this is to be found in the fact that wood consists essentially of carbon, hydrogen, and oxygen; and the sulphuric acid abstracts the hydrogen and oxygen, leaving the carbon mainly in the uncombined state. Similarly it abstracts moisture from gases, and it is used extensively in the laboratory for this purpose. In contact with the skin it acts as upon wood, causing wounds which are painful and difficult to heal.

Sulphuric acid is what is called a strong acid, a term which needs further explanation, and the subject of the relative strengths of acids will be discussed in due time. As used here, it means simply that the acid has the power to decompose the salts of most other acids, appropriating the metals and setting the other acids free. This is illustrated by the formation of hydrochloric and nitric acids by treating sodium chloride and potassium nitrate respectively with sulphuric acid. We shall see, however, that the fact that sulphuric acid decomposes the salts of hydrochloric and nitric acids does not prove that it is a stronger acid than they are. There are other facts besides the strengths of the acids which determine whether such decompositions take place or not.

Sulphuric acid gives up its oxygen to other substances

comparatively easily, and is generally reduced to sulphurous acid which is decomposed into sulphur dioxide and water. Thus hydrogen sulphide and hydrobromic acid both act upon it, as we have seen ; the products being, in the former case, sulphur dioxide, water, and sulphur ; in the latter, sulphur dioxide, water, and bromine :

$$H_2SO_4 + H_2S \quad = 2H_2O + SO_2 + S;$$
$$H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2.$$

Generally, in acting upon metals it forms the corresponding salt and hydrogen is given off, but if the temperature is high and the acid concentrated the hydrogen acts upon the acid, reducing it. Thus, in making hydrogen by treating zinc with sulphuric acid, if the acid is dilute and is kept cool the reaction takes place in the simplest way ; but if the acid is concentrated and is allowed to get hot some hydrogen sulphide is always formed. Copper does not act upon sulphuric acid at ordinary temperatures. If it is treated with concentrated sulphuric acid, sulphur dioxide is the chief reduction-product. Even free hydrogen if passed into sulphuric acid heated to 160° reduces it, forming sulphur dioxide. The complete reduction of sulphuric acid to sulphur and hydrogen sulphide is beautifully shown by the action of hydriodic acid. As was stated in speaking of the action of sulphuric acid upon potassium iodide, four reactions may take place when these substances act upon each other. They are represented by the equations

$$2KI \quad + H_2SO_4 = K_2SO_4 + 2HI;$$
$$H_2SO_4 + 2HI \quad = 2H_2O \quad + SO_2 + 2I;$$
$$H_2SO_4 + 6HI \quad = 4H_2O \quad + S \quad + 6I;$$
$$H_2SO_4 + 8HI \quad = 4H_2O \quad + H_2S + 8I.$$

Carbon and sulphur also act upon sulphuric acid and reduce it to sulphur dioxide. With sulphur the action is represented thus :

$$2H_2SO_4 + S = 3SO_2 + 2H_2O.$$

Sulphuric acid is a dibasic acid (see p. 138) and forms two series of salts, normal salts of the general formula $M_2SO_4$, and acid salts of the formula $MHSO_4$. The sulphates are very stable salts. Those of the strongest bases are not decomposed by the highest heat. Those of weaker bases break down, giving up sulphur trioxide ; or if the decomposition takes place at a temperature above that at which sulphur trioxide breaks down, this decomposes into sulphur dioxide and oxygen.

**Tetrahydroxyl-Sulphuric Acid, $OS(OH)_4$.**—This compound has already been referred to as being formed by the addition of water to ordinary sulphuric acid. It is a crystallized compound which melts at 7.5°. No salts of this acid are known, or, rather, no salts derived from it by the replacement of all the hydrogen by metal are known. Only two of the hydrogen atoms appear to be replaceable. This compound is generally represented by the formula $H_2SO_4 + H_2O$, and called a hydrate.

**Normal Sulphuric Acid, $S(OH)_6$.**—This is commonly represented by the formula $H_2SO_4 + 2H_2O$ and, like the preceding compound, regarded as a hydrate. It appears to be formed by the action of water on sulphuric acid. On mixing sulphuric acid and water the maximum contraction takes place when the quantities necessary to form this compound are brought together, and there are other good reasons for believing that the compound exists in the solution. It is not a solid like the preceding compound. The acid forms no salts bearing simple relations to it. There are some salts known, however, which appear to be related to it, as, for example, the salt $K_3HS_2O_8$ and some others similar to it. The acid from which these salts are derived is believed to be formed from the normal acid by elimination of water, as represented below :

$$\genfrac{}{}{0pt}{}{HO}{HO}{>}S\left\{\begin{matrix} OH \\ OH \\ OH \\ OH \end{matrix} + \begin{matrix} HO \\ HO \\ HO \\ HO \end{matrix}\right\}S<\genfrac{}{}{0pt}{}{OH}{OH} = (HO)_2OS<\genfrac{}{}{0pt}{}{O}{O}>SO(OH)_2 + 4H_2O.$$

An acid formed in this way would have the formula

$H_4S_2O_8$, and the salt $K_3HS_2O_8$ is the tertiary potassium salt of this acid.

**Disulphuric Acid, Pyrosulphuric Acid, $H_2S_2O_7$.**—This compound, which is also known by the names *fuming sulphuric acid* and *Nordhausen sulphuric acid*, is closely related to ordinary sulphuric acid, and is made from it by treating it with sulphur trioxide, the two combining directly, as represented thus:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

It is made by distilling ferrous sulphate which is not perfectly dry:

$$4FeSO_4 + H_2O = 2Fe_2O_3 + 2SO_2 + H_2S_2O_7.$$

A so-called *solid sulphuric acid* is now manufactured by a process which will be referred to under Sulphur Trioxide. It is essentially disulphuric acid.

Disulphuric acid, as it is found in the market, is generally a thick liquid which gives off dense fumes when exposed to the air, and breaks down completely into sulphur trioxide and sulphuric acid when heated. When pure it crystallizes in large crystals which melt at 35°.

It is believed that the relation between disulphuric acid and ordinary sulphuric acid should be expressed by these formulas:

$$O_2S{<}^{OH}_{OH} + {}^{HO}_{HO}{>}SO_2 = O_2S{\overset{O}{\underset{OH\ HO}{<\ >}}}SO_2 + H_2O.$$

Or the formula of the acid may be written thus:

$$\begin{array}{c} O_2S{-}OH \\ | \\ O \\ | \\ O_2S{-}OH. \end{array}$$

This relation is similar to that believed to exist between the normal acid $S(OH)_6$ and the acid $H_4S_2O_9$ (see p. 218).

Disulphuric acid forms normal salts of the general formula $M_2S_2O_7$ and acid salts of the general formula $MHS_2O_7$. When heated the normal salts break down, yielding ordinary sulphates and sulphur trioxide:

$$M_2S_2O_7 = M_2SO_4 + SO_3.$$

When an acid sulphate like $KHSO_4$ is heated to a sufficiently high temperature it breaks down into water and a disulphate:

$$2KHSO_4 = K_2S_2O_7 + H_2O.$$

**Sulphurous Acid, $H_2SO_3$.**—While no acid of the formula $H_2SO_3$ is known in the free condition, a large number of salts which are derived from this acid are known. They are made by treating a water solution of sulphur dioxide with bases, and therefore it is believed that the solution contains the acid which is formed by the action of sulphur dioxide on water, thus:

$$SO_2 + H_2O = H_2SO_3.$$

It is, however, so unstable that it breaks down into the dioxide and water at every attempt to isolate it. The dioxide, as has been stated and as will be shown more fully, is formed by the burning of sulphur and by the reduction of sulphuric acid. The acid forms a number of unstable hydrates, apparently of complicated composition. Owing to their great instability, however, the investigation of these substances is extremely difficult and unsatisfactory.

Sulphurous acid takes up oxygen readily and is thus transformed into sulphuric acid. It is only necessary to allow a solution to stand for a time to find that the odor of the gas disappears and that sulphuric acid is then present in the solution. Sulphurous acid is frequently used in the laboratory as a reducing agent. Its action in this way has been illustrated in the method for the extraction of selenium from selenious acid (see p. 203). The reaction in this case is represented thus:

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4 \, ; \text{ or}$$
$$H_2SeO_3 + 2H_2SO_3 \quad = Se + 2H_2SO_4 + H_2O.$$

Another illustration of its power as a reducing agent is shown in its action upon iodic acid. When it is added to a solution containing iodic acid, $HIO_3$, iodine separates, the reaction taking place in accordance with the following equation:

$$2HIO_3 + 5H_2SO_3 = H_2O + 5H_2SO_4 + I_2.$$

If sulphurous acid is added to the liquid in which the iodine is suspended further action takes place, the iodine being reduced to hydriodic acid, thus:

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$

This reaction takes place only in dilute solution. Concentrated sulphuric acid acts upon hydriodic acid and is reduced by it, as we have seen. Towards some substances sulphurous acid acts as an oxidizing agent, and is itself reduced to lower forms, as hyposulphurous acid, $H_2S_2O_4$, and hydrogen sulphide. This has been illustrated in the action of hydriodic acid upon sulphuric acid. It is also illustrated in the action of zinc upon sulphurous acid in the presence of hydrochloric acid, when this reaction takes place:

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + 3H_2O + H_2S.$$

Treated with zinc alone the acid sodium salt, $NaHSO_3$, is reduced as shown in the following equation, a salt of hyposulphurous acid, $H_2S_2O_4$, being formed:

$$Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + Na_2S_2O_4 + 2H_2O.$$

Sulphurous acid when heated in a sealed tube breaks down into sulphuric acid and sulphur:

$$3H_2SO_3 = 2H_2SO_4 + H_2O + S.$$

This kind of decomposition is also characteristic of the

salts of the acid with the alkali metals, as, for example, sodium sulphite :

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

In fact, whenever an alkali salt of any of the oxygen acids of sulphur is heated the tendency is towards the formation of the sulphate, all the oxygen in the salt going to form sulphate ; and the other elements in excess of what may be needed for the sulphate arranging themselves in other forms.

Just as the sulphites take up oxygen to form sulphates, they also take up sulphur to form thiosulphates. The two reactions appear to be perfectly analogous :

$$Na_2SO_3 + O = Na_2SO_4 ;$$
$$Na_2SO_3 + S = Na_2S_2O_3 \text{ (or } Na_2SO_3S).$$

Sulphurous acid forms two series of salts, the normal sulphites of the general formula $M_2SO_3$, and the acid sulphites of the general formula $MHSO_3$. These are unstable, though not as markedly so as the acid itself. When treated with most acids they are decomposed, yielding sulphur dioxide instead of sulphurous acid. The decomposition of sodium sulphite with hydrochloric acid is represented by the equation

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2 ;$$

with sulphuric acid thus :

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

The sulphites, like sulphurous acid, combine readily with oxygen, tending to pass over into the sulphates, and, as has been remarked, they also tend to unite with sulphur to form the thiosulphates.

**Hyposulphurous Acid, $H_2S_2O_4$.**—This acid is also called hydrosulphurous acid, but the name hyposulphurous acid is more in accordance with the nomenclature adopted for the other acids, and is now preferred. But little is

known of the compound. It is formed by reduction of a salt of sulphurous acid by treating with zinc, when this reaction takes place:

$$Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + Na_2S_2O_3 + 2H_2O.$$

The free acid cannot be obtained from this sodium salt, and notwithstanding the fact that it has been the subject of a number of elaborate investigations there is still some doubt as to the composition of the salt, the discoverer still claiming that it has the composition represented by the formula $Na_2SO_2$, according to which it is to be referred to an acid of the formula $H_2SO_2$.

Hyposulphurous acid, like sulphurous acid, combines readily with oxygen, and passes first into sulphurous and then into sulphuric acid. Its reducing action is stronger than that of sulphurous acid. It is decomposed by standing in the air, yielding first thiosulphuric acid, $H_2S_2O_3$, and then sulphur dioxide, sulphur, and water.

Hyposulphurous acid, so far as composition is concerned, occupies a position between thiosulphuric acid, $H_2S_2O_3$, and pyrosulphurous acid, $H_2S_2O_5$, which latter is related to sulphurous acid in the same way that disulphuric or pyrosulphuric acid, $H_2S_2O_7$, is related to sulphuric acid. The relations between hyposulphurous, thiosulphuric, and pyrosulphurous acids are shown in the table below:

$$H_2S_2O_3;$$
$$H_2S_2O_4;$$
$$H_2S_2O_5.$$

**Thiosulphuric Acid, $H_2S_2O_3$.**—This acid was formerly, and is still by many, called hyposulphurous acid. Its formation, or the formation of its salts by the addition of sulphur to the sulphites, has been mentioned, and the analogy between this reaction and that of the formation of sulphates by the addition of oxygen to sulphites has been commented upon. It may be regarded as sulphuric acid in which sulphur has been substituted for one atom

of oxygen, and hence the name thiosulphuric acid is appropriate, whereas the name hyposulphurous acid suggests at once a compound similar to sulphurous acid, but containing less oxygen, and is therefore inappropriate. Sodium thiosulphate is formed together with the pentasulphide by the action of sulphur upon sodium hydroxide :

$$6\text{NaOH} + 12\text{S} = 2\text{Na}_2\text{S}_5 + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}.$$

The sulphides of the alkali metals pass over into the corresponding thiosulphates by the action of oxygen. Thus the pentasulphide is changed when exposed to the air in aqueous solution. The action consists in a substitution of three atoms of oxygen for three of sulphur :

$$\text{Na}_2\text{S}_5 + 3\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 3\text{S}.$$

Sodium thiosulphate is formed, further, by the action of iodine upon a mixture of sodium sulphide and sodium sulphite :

$$\text{S}\!<\!^{\text{Na}}_{\text{Na}} \atop \text{O}_3\text{S}\!<\!^{\text{Na}}_{\text{Na}} + 2\text{I} = \text{S}\!<\!^{\text{Na}} \atop \text{O}_3\text{S}\!>\!_{\text{Na}} + 2\text{NaI}.$$

The acid itself is very unstable, breaking down into sulphur dioxide, sulphur, and water (see p. 190). By acids its salts are decomposed in a similar way with evolution of sulphur dioxide and separation of sulphur, which appears suspended in the liquid in a very fine state of division. With hydrochloric acid the decomposition takes place thus :

$$\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} = 2\text{NaCl} + \text{SO}_2 + \text{S} + \text{H}_2\text{O}.$$

When heated the thiosulphate of sodium breaks down according to the rule stated in speaking of the decomposition of the sulphite by heat. All the oxygen goes to the formation of the sulphate, and the elements left over

in excess of what is required for the sulphate unite to form another compound, thus :

$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5.$$

**Other Acids of Sulphur.**—Of the other acids of sulphur but little need be said here. As was stated on page 208, these acids form a series the members of which are closely related to one another. The series is as follows :

| | | |
|---|---|---|
| Dithionic acid, | . . . . . . . | $H_2S_2O_6$ |
| Trithionic acid, | . . . . . . . | $H_2S_3O_6$ |
| Tetrathionic acid, | . . . . . . | $H_2S_4O_6$ |
| Pentathionic acid, | . . . . . . | $H_2S_5O_6$ |

*Dithionic Acid,* or a salt of the acid, is made by passing sulphur dioxide into water having finely powdered manganese dioxide in suspension. This reaction takes place :

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

The product is the manganese salt of dithionic acid, and from this other salts can be prepared. The free acid breaks down readily into sulphuric acid and sulphur dioxide :

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

So, too, when a salt of the acid is heated it breaks down, forming a sulphate and sulphur dioxide :

$$K_2S_2O_6 = K_2SO_4 + SO_2.$$

*Trithionic Acid,* $H_2S_3O_6$, or its potassium salt, is formed by treating a solution of acid potassium sulphite, $KHSO_3$, with "flowers of sulphur," when reaction takes place thus :

$$6KHSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

When the dry potassium salt is heated it is de-

composed, yielding the sulphate, sulphur dioxide, and sulphur :

$$K_2S_3O_6 = K_2SO_4 + SO_2 + S.$$

Similarly, when treated with acids, decomposition takes place with evolution of sulphur dioxide, separation of sulphur, and formation of sulphuric acid :

$$H_2S_3O_6 = H_2SO_4 + SO_2 + S.$$

*Tetrathionic Acid,* $H_2S_4O_6$, is made from salts of thio-sulphuric acid by treating them with iodine.  Thus with sodium thiosulphate the reaction is

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$

The acid is moderately stable, so that a dilute solution can be boiled without undergoing decomposition.  When the concentrated acid is heated, however, it breaks down into sulphuric acid, sulphur dioxide, and sulphur :

$$H_2S_4O_6 = H_2SO_4 + SO_2 + 2S.$$

*Pentathionic Acid,* $H_2S_5O_6$, is formed by the action of hydrogen sulphide upon a solution of sulphur dioxide in water.

**Persulphuric Acid,** $H_2S_2O_8$, is formed by dissolving the oxide $S_2O_7$ in water, the oxide itself being formed by subjecting a mixture of sulphur dioxide and oxygen to the silent discharge in an ozone tube (see p. 85).  The potassium salt of persulphuric acid is easily obtained by subjecting to electrolysis a saturated solution of acid potassium sulphate.

**Constitution of the Acids of Sulphur.**—The existence of the oxide $SO_3$ and of the iodide $SI_6$ seems to show that sulphur is sexivalent towards oxygen and towards iodine. Considering, further, the facts presented under the head of Periodic Acid (which see), which can only be explained satisfactorily by the aid of the assumption that the different varieties of periodic acid are derived from the normal acid $I(OH)_7$, and the analogous facts presented under Sul-

phuric Acid, which lead to the belief that this acid is de-
rived from the normal acid S(OH)$_6$, the arguments in favor
of the sexivalence of sulphur in sulphuric acid are seen
to be strong, though not conclusive. On the other hand, if
sulphur is sexivalent in sulphur trioxide and in sulphuric
acid, it is quadrivalent in sulphur dioxide and sulphur
tetrachloride, and bivalent in hydrogen sulphide and sul-
phur dichloride. But if sulphur is sexivalent in sul-
phuric acid the constitution of the acid must be repre-

$$\text{sented by the formula } \begin{array}{c} O \\ \| \\ H-O-S-O-H \\ \| \\ O \end{array} \text{ or } S \left\{ \begin{array}{l} OH \\ OH \\ O \\ O \end{array} \right. . \text{ Of}$$

course such a formula as this involves the hypothesis
that when an oxygen atom is combined with only one
other atom two valences or affinities are brought into
play, and in regard to this we have very little if any evi-
dence. It may be said, however, that if oxygen which
is thus combined is replaced by univalent atoms its
place is always taken by two of these, indicating that
whatever the power may be which holds the oxygen atom
in combination, that same power can hold two chlorine
atoms, etc., and it is convenient to use the double line to
indicate the existence of this power.

The view expressed by the above formula in regard to
the structure of sulphuric acid has been tested experi-
mentally by methods which appear somewhat compli-
cated, but the principle involved can be easily explained.
If the formula is correct, then both hydroxyl groups bear
the same relation to the sulphur, and so also do the two
hydrogen atoms. Whether one or the other of these hy-
drogen atoms be replaced by another atom or group of
atoms, the same product should result. Or, if one of the
hydrogen atoms is replaced by one group and the other
by another group, it should make no difference in which
order the two groups are introduced. The product should
be the same in the two cases. Thus, suppose one hydro-
gen atom is replaced by a group X, and the other by Y,
the product should be represented by the formula

$$Y-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-X \quad \text{in one case, and by} \quad X-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-Y \quad \text{in the}$$

other case. But if the formula given for sulphuric acid is correct the two compounds are identical. By methods which involve the use of apparently complex organic compounds the two hydrogen atoms have been thus replaced by two different groups, first in one way and then in the reverse order; and the two products have been found to be identical. Further, it has been shown that when the two hydroxyl groups of sulphuric acid are replaced by chlorine, forming the compound $S\begin{cases} Cl \\ Cl, \text{ and} \\ O_2 \end{cases}$ the chlorine atoms then replaced by certain groups of atoms, these groups are in direct combination with sulphur and not with oxygen. All the evidence points to the conclusion that the view represented above is correct.

In attempting to determine the constitution of sulphurous acid a new difficulty arises. Just as hydrogen which is in combination with oxygen is replaceable by metals, or is acidic, so, also, is hydrogen which is in combination with sulphur. It is possible, therefore, to conceive of two arrangements of the atoms composing sulphurous acid, both representing dibasic acids. One of these arrangements is this, $O=\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{S}}-O-H$, in which the sulphur is represented as sexivalent; the other is this, $H-O-\overset{\overset{O}{\|}}{S}-O-H$, in which the sulphur is represented as quadrivalent. The facts that sulphurous acid is formed so readily by simple contact of sulphur dioxide with water; that it breaks down as readily into sulphur dioxide and water; and that it takes up oxygen and sulphur so readily to form sulphuric and thiosulphuric acids, seem to speak in favor of the second of the above formulas. But, on the

other hand, certain facts established in the study of the organic derivatives of sulphurous acid form a strong argument in favor of the first formula. It is possible by means of reactions with certain compounds of carbon to replace one of the metal atoms in a sulphite in such a way as to produce a compound of the formula $S\begin{cases} R \\ ONa, \\ O_2 \end{cases}$ the conduct of which is such as to show that in it the group R is in direct combination with sulphur. As the compound is formed apparently by direct replacement of a sodium atom in the sulphite it appears that this sodium atom was in combination with sulphur. Further, when the second sodium is replaced by the group R a compound of the formula $S\begin{cases} R \\ OR \\ O_2 \end{cases}$ is obtained, in which it appears that one of the groups is in combination with sulphur and the other with oxygen. Now, it is possible by starting with the compound $S\begin{cases} Cl \\ Cl \\ O \end{cases}$ which is made, as we shall see, by replacing one oxygen atom of sulphur dioxide by two chlorine atoms, to introduce in the place of the two chlorine atoms two groups, OR, and thus obtain the compound $S\begin{cases} OR \\ OR \\ O \end{cases}$ which plainly has the same composition as the one represented by the formula $S\begin{cases} R \\ OR \\ O_2 \end{cases}$ but it has a different constitution. It was found by experiment that the two compounds have different properties, and it seems probable, therefore, that the two formulas given represent the structure of the two compounds. As the one which has one group R in combination with sulphur is obtained from sodium sulphite by replacement of sodium, the conclusion seems to be justified that sulphurous acid has the constitution represented

by the formula

$$O = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{S}} = O \quad \text{or} \quad S \left\{ \begin{array}{l} H \\ OH, \\ O_2 \end{array} \right. \text{which may also be}$$

written $O_2S <^H_{OH}$. At the same time it appears quite possible that a sulphurous acid of the other constitution, $OS <^{OH}_{OH}$, may be found, as there are innumerable examples furnished by chemistry of the existence of two or more compounds of the same percentage composition but different constitution. Two or more substances having the same composition but different constitution are said to be *isomeric.* Although examples of isomerism are rare among the compounds of most elements, yet among the compounds of carbon they are met with in large numbers, and in studying these compounds a great deal of attention has been paid to the phenomena of isomerism. It is possible that the second form of sulphurous acid cannot exist on account of the tendency of sulphur to act as a sexivalent element. This is, however, mere speculation, and, unless the suggestion can be tested experimentally, it is of very little value. If sulphurous acid has the constitution above assigned to it then the transformation of sulphurous acid into sulphuric acid is not simply a direct combination of oxygen with sulphur, but the act must involve a partial breaking down of the sulphurous acid and a recombination of the constituents thus:

$$H-O-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O}{||}}{S}}-H + O = H-O-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O}{||}}{S}}-O-H.$$

If this view is correct the oxygen displaces the hydrogen and then combines with it and the sulphur.

If the action takes place in the same way with sulphur it must be represented thus:

$$\text{H-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{-H} + \text{S} = \text{H-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{-S-H};$$

and, according to this, the formula $\text{H-O-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{-S-H}$ repre-

sents the structure of thiosulphuric acid. The same con-
clusion regarding the structure of thiosulphuric acid is
reached by a consideration of one of the methods by
which its sodium salt is made. This is the method which
consists in treating a mixture of sodium sulphide and
sodium sulphite with iodine. The iodine simply extracts
two atoms of sodium from the two molecules, and it
seems probable that the residues of the two molecules
unite. If this is correct the following equation represents
what takes place :

$$\overset{\displaystyle \text{S} <^{\text{Na}}_{\text{Na}}}{\underset{\displaystyle \underset{\underset{\text{O}}{\|}}{\text{O=S-O-Na}}}{\text{Na}}} + 2\text{I} = \overset{\displaystyle \text{S-Na}}{\underset{\displaystyle \underset{\underset{\text{O}}{\|}}{\text{O=S-O-Na}}}{|}} + 2\text{NaI};$$

and the constitution of thiosulphuric acid is represented
by the formula $\overset{\displaystyle \text{S-H}}{\underset{\displaystyle \underset{\underset{\text{O}}{\|}}{\text{O=S-O-H}}}{|}}$, which is identical with that

given above. This latter method, however, it should be
remarked, might also be used as an argument in favor of
the constitution $\overset{\displaystyle \text{H}}{\underset{\displaystyle \underset{\underset{\text{O}}{\|}}{\text{O=S-O-S-H}}}{|}}$ for thiosulphuric acid ; for

if, when the iodine acts upon the sulphite, it extracts the
sodium atom which is in combination with oxygen, then
the union of the two residues would, in all probability,

take place at this point, and the constitution of the acid would be that represented by the last formula given. It will be seen that our knowledge in regard to the structure of thiosulphuric acid is very unsatisfactory.

The same remark may be made in regard to our knowledge of the structure of the other acids of sulphur. The method used in making the salts of tetrathionic acid is suggestive, and if we knew the structure of thiosulphuric acid, we might draw a conclusion in regard to that of tetrathionic acid. The method consists in treating the sodium salt of thiosulphuric acid with iodine. It appears probable that of the two formulas above given for thio-

$$\underset{\underset{\overset{\|}{O}}{\overset{\overset{\|}{O}}{}}}{}$$

sulphuric acid this one, H–S–S–O–H, is to be preferred,

for the reason that it is more probable that when iodine acts upon sodium thiosulphate it removes the sodium atom which is in combination with sulphur, than that it removes the one which is in combination with oxygen. If this is true the above formula for thiosulphuric acid follows. Now, further, reasoning in the same way, it appears probable that when iodine acts upon sodium thiosulphate it removes the sodium which is in combination with sulphur, and in this case the formation of tetrathionic acid must be represented in the following way:

$$\underset{\overset{\|}{O}}{Na\text{-}O\text{-}\overset{\overset{O}{\|}}{S}\text{-}S\text{-}}\begin{vmatrix} Na + Na \\ \hline I \quad\quad I \end{vmatrix}\text{-}\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}\text{-}S\text{-}O\text{-}Na = Na O\text{-}\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}\text{-}S\text{-}S\text{-}\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}\text{-}O\text{-}Na + 2NaI.$$

According to this, in tetrathionic acid there are four sulphur atoms in combination by one affinity each. This compound is, however, comparatively stable, while thiosulphuric acid, in which a similar combination of only two sulphur atoms is assumed, is extremely unstable. What value to attach to such considerations as these we do not know.

**Compounds of Sulphur with Oxygen.**—Sulphur, as has been repeatedly stated, combines with oxygen in two pro-

portions, forming the oxides $SO_2$ and $SO_3$, or sulphur dioxide and sulphur trioxide. Besides these two it also forms a *sesquioxide*, $S_2O_3$, and a *heptoxide*, $S_2O_7$, but comparatively little is known in regard to the last two. The one best known is sulphur dioxide.

**Sulphur Dioxide, $SO_2$.**—This, as has been seen, is formed when sulphur is burned in the air or in oxygen; and it is also easily formed by reduction of the higher oxides and acids of sulphur. Owing to the fact that with water it forms sulphurous acid, it is frequently called sulphurous anhydride. The methods for making it were referred to under sulphuric acid, and the reactions involved were discussed then with a sufficient degree of fulness. It need only be said here that in the laboratory the methods most commonly employed are: (1) Heating sulphuric acid with copper; (2) heating the acid with carbon (charcoal); and (3) heating the acid with sulphur. When carbon is used two gases are formed, viz., carbon dioxide and sulphur dioxide:

$$2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O.$$

The gas can also be made by heating a mixture of a metallic oxide and sulphur. Thus, when cupric oxide and sulphur are heated together this reaction takes place:

$$2CuO + 2S = Cu_2S + SO_2.$$

Sulphur dioxide is a colorless, transparent gas, which has a pungent, suffocating odor, familiar as the odor of burning sulphur matches. It is poisonous, causing death when inhaled in any quantity, and giving rise to bad symptoms even in comparatively small quantities. It does not readily give up its oxygen, so that burning bodies are extinguished when introduced into it. It acts something like water in this respect. It is more than twice as heavy as air, its specific gravity being 2.26. When sulphur is burned in oxygen gas the sulphur dioxide formed occupies the same volume as the oxygen used up, so that there is no change in the volume. This

can be shown by the experiment here described. In a
bent glass tube, of the form shown in Fig. 8, there is

placed a piece of sulphur, and the
tube is then half filled with pure
oxygen over mercury. On now
heating the tube at the part where
the sulphur is, this burns and is
converted into sulphur dioxide.
After the tube has cooled down to
the ordinary temperature the gas is
found to occupy the same volume as before. This will
be readily understood by the aid of the following con-
siderations: In the reaction

$$S + O_2 = SO_2$$

one molecule of sulphur dioxide is formed for every
molecule of oxygen used up. But a molecule of sulphur
dioxide in the form of gas occupies the same space as a
molecule of oxygen, so that, as the space occupied by the
sulphur in the experiment is insignificant, there is no
change in volume occasioned by the above reaction.

Sulphur dioxide dissolves in water, as we have seen,
and forms a liquid in which, judging by its conduct, sul-
phurous acid is present.

The gas is easily liquefied by cold alone. It is only
necessary for this purpose to pass the dry gas through a
tube surrounded by a freezing mixture of ice and salt.
The liquid changes rapidly into gas under ordinary pres-
sure at the ordinary temperature. In this change so
much heat is absorbed that a temperature of about − 60°
can be produced by means of it; and a portion of the
liquid can be solidified.

Sulphur dioxide is very stable. If heated to 1200°
under pressure, however, it breaks down into sulphur
trioxide and sulphur:

$$3SO_2 = 2SO_3 + S.$$

When conducted into solutions of bases or of carbonates
the corresponding sulphites are formed:

*(Figure caption: FIG. 8.)*

$$2KOH + SO_2 = K_2SO_3 + H_2O \,;$$
$$K_2CO_3 + SO_2 = K_2SO_3 + CO_2.$$

Under certain conditions, as when the gas is passed into a hot solution of an alkali carbonate, a salt of the general formula $M_2S_2O_5$ is formed. This bears to the sulphite the same relation that the pyrosulphate bears to the sulphate:

$$2KHSO_3 = K_2S_2O_5 + H_2O \,;$$
$$\text{and } 2KHSO_4 = K_2S_2O_7 + H_2O.$$

Sulphur dioxide is used extensively for the purpose of bleaching silk, wool, straw, and basket-ware. In order that it may bleach, however, water must be present, so that it appears that the true bleaching agent in this case is sulphurous acid and not the dioxide. When we consider that sulphur dioxide does not readily take up nor give up oxygen, while sulphurous acid does readily take it up, the necessity of having water present in the bleaching process at once becomes apparent. The bleaching in some cases certainly consists in abstracting oxygen from the colored substances, and thus converting them into colorless products. In other cases it is due to the formation of compounds of sulphurous acid with the dye-stuffs.

Sulphur dioxide is not only a bleaching agent like chlorine, but like chlorine it is also a disinfectant. It has to some extent the power to destroy the organisms which cause changes in organic substances. It prevents fermentation and is therefore used as a preservative. Its power to destroy the germs of disease, that is, to disinfect, is not as great as is frequently supposed. Much larger quantities are necessary for this purpose than are commonly used.

**Sulphur Trioxide, $SO_3$.**—This compound is made by passing sulphur dioxide and oxygen together over heated platinum in a finely divided state. It is obtained most readily by heating disulphuric acid, which breaks up

easily into sulphur trioxide and ordinary sulphuric acid according to the equation

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

Similarly, the acid sulphates of the alkali metals yield the corresponding normal sulphates and sulphur trioxide :

$$2NaHSO_4 = Na_2SO_4 + SO_3 + H_2O.$$

It is now manufactured on the large scale by passing sulphur dioxide and oxygen together over asbestos covered with finely divided platinum, and the product thus obtained is passed into ordinary sulphuric acid for the purpose of making " solid sulphuric acid " which, as has been stated, is almost pure disulphuric acid, $H_2S_2O_7$.

Sulphur trioxide is a white crystallized solid which appears to exist in two modifications. The one is a liquid at ordinary temperatures, but it solidifies at about 16°. According to the latest investigations there is but one modification of the oxide. It is a solid which melts at 14.8°, forming a liquid which boils at 46°. In contact with the air the oxide gives off thick fumes which are partly due to the great power of the compound to combine with water. Water acts with violence upon it, the heat evolved in the act being 39,170 cal. It also acts upon substances containing hydrogen and oxygen in much the same way that concentrated sulphuric acid does, charring them by abstracting the hydrogen and oxygen. It acts, however, more violently in this way than sulphuric acid does. With water it forms sulphuric acid, and it is, therefore, called sulphuric anhydride. The reaction involved in passing from sulphur trioxide to sulphuric acid is of a kind which, as we have seen, is frequently met with both with acidic oxides or anhydrides, and with basic or metallic oxides ; and it is desirable that it should here be studied a little more carefully than it has yet been. What we know is that when sulphur trioxide acts upon water there is a great deal of heat evolved, and compounds of different composition are obtained. The composition of these compounds is represented by the formu-

las $SO_3 + H_2O$, $SO_3 + 2H_2O$, and $SO_3 + 3H_2O$. So, too, when calcium oxide or lime, $CaO$, acts upon water, there is great evolution of heat, and a compound is formed the composition of which is represented by the formula $CaO + H_2O$. But these formulas do not attempt to give any account of what takes place in the chemical acts referred to. That the water is not present in the compounds as water seems evident, in the first place from the conduct of the compounds, and in the second place from the amount of heat evolved in the act of combination. Now, taking the chemical conduct of the substances into consideration, they appear to contain hydrogen in combination with oxygen, and their conduct becomes comprehensible on the supposition that the group known as hydroxyl, (–O–H), is present. This view has been found to be in accordance with a large number of facts, and it is of great assistance in dealing with these facts. The view is distinctly this : When an acidic oxide acts upon water it is converted into a hydroxyl compound which has acid properties, as shown in this equation :

$$O=\overset{\overset{\textstyle O}{\textstyle \|}}{S}=O \;+\; \begin{matrix} H_2O \\ H_2O \\ H_2O \end{matrix} \;=\; S \begin{cases} OH \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases}$$

According to this, each molecule of water is decomposed and each hydrogen atom in the resulting compound is in combination with oxygen. The same kind of action takes place in the case of some basic oxides, as shown, for example, in the case of calcium oxide :

$$Ca=O + H_2O = Ca{<}{\begin{matrix} O-H \\ O-H \end{matrix}}.$$

By means of certain reagents which will be taken up later it is possible to replace oxygen in compounds by chlorine, two chlorine atoms taking the place of one oxygen atom. So, also, when the oxygen of the hydroxides is replaced by chlorine, the result is that each

hydroxyl group is replaced by one atom of chlorine. This is easily understood. For, if in calcium hydroxide each oxygen atom should be replaced by two chlorine atoms, the result would be a combination of atoms represented thus, $Ca < {ClCl-H \atop ClCl-H}$, and from this, hydrochloric acid would be given off, leaving calcium chloride:

$$Ca < {ClClH \atop ClClH} = Ca < {Cl \atop Cl} + 2HCl.$$

The result, therefore, of treating the hydroxide $Ca < {O-H \atop O-H}$ in such a way as to replace each of the two oxygen atoms by two chlorine atoms is the formation of a compound $Ca < {Cl \atop Cl}$, which is derived from the hydroxide by replacing each hydroxyl group by one atom of chlorine. These facts lend support to the hydroxyl hypothesis.

Just as sulphur trioxide acts upon water to form sulphuric acid, so it acts upon metallic oxides, forming sulphates. Thus with calcium oxide it forms calcium sulphate:

$$CaO + SO_3 = CaSO_4.$$

It combines also with hydrochloric acid, forming the compound $SO_3HCl$. The action in this case is analogous to that which takes place with water, and is represented thus:

$$O=\overset{\overset{\textstyle O}{\|}}{S}=O + H-Cl = O=\underset{\underset{\textstyle Cl}{|}}{\overset{\overset{\textstyle O}{\|}}{S}}-O-H.$$

The analogy between this and the action with water will be apparent by a consideration of the following equation:

$$O=\overset{\overset{\textstyle O}{\|}}{S}=O + H-O-H = O=\underset{\underset{\textstyle H}{|}}{\underset{\underset{\textstyle O}{|}}{\overset{\overset{\textstyle O}{\|}}{S}}}-O-H.$$

The chlorine compound appears to be ordinary sulphuric acid in which one hydroxyl group has been replaced by a chlorine atom. When the compound is treated with water hydrochloric acid is given off and sulphuric acid is formed, thus :

$$S \begin{cases} Cl \\ OH \\ O_2 \end{cases} + HOH = S \begin{cases} OH \\ OH \\ O_2 \end{cases} + HCl.$$

**Acid Chlorides of Sulphur.**—In the introduction to this chapter reference was made to certain compounds which sulphur forms with oxygen and chlorine, known as acid chlorides, because when brought in contact with water they form acids. Strictly speaking, all the compounds of sulphur and chlorine are of this order ; the name is, however, generally applied to those compounds which are derived from the acids by replacement of the hydroxyl by chlorine. Thus the acid chloride of sulphuric acid is $SO_2 <^{Cl}_{Cl}$, which is plainly sulphuric acid in which the two hydroxyl groups have been replaced by chlorine. So, also, the compound $SO <^{Cl}_{Cl}$ is related in the same way to a sulphurous acid of the formula $SO <^{OH}_{OH}$, which, however, does not appear to be ordinary sulphurous acid. But the existence of the compounds $SO_2 <^{Cl}_{Cl}$ and $SO <^{Cl}_{Cl}$, which are to be regarded respectively as sulphuric and sulphurous acids in which both hydroxyls are replaced by chlorine, suggests the existence of the two compounds $SO_2 <^{Cl}_{OH}$ and $SO <^{Cl}_{OH}$, derived from the acids by the replacement of one hydroxyl in each by chlorine. The former compound is known, the latter is not.

**Thionyl Chloride, SOCl₂,** can be made from sulphur dioxide by replacing one oxygen atom by two chlorine atoms. This is effected by treating sulphur dioxide with phosphorus pentachloride, $PCl_5$, a compound which readily gives up a part or all of its chlorine and takes up

oxygen in its place, and is therefore extensively used in chemistry for the purpose of replacing oxygen by chlorine. With sulphur dioxide the reaction takes place thus:

$$SO_2 + PCl_5 = SOCl_2 + POCl_3.$$

The compound is also formed by treating sodium sulphite with phosphorus pentachloride, when this reaction takes place:

$$SO(ONa)_2 + 2PCl_5 = SOCl_2 + 2NaCl + 2POCl_3.$$

In order to understand this reaction it appears necessary that sodium sulphite should be represented by the formula given, which, as will be seen, is not in accordance with the conclusion reached regarding the structure of sulphurous acid. It may be that the reaction is more complicated than here represented, and that sulphur dioxide is first given off, and that this then acts upon the pentachloride.

Thionyl chloride is a liquid with a strong characteristic odor. It acts readily upon water, forming sulphur dioxide and hydrochloric acid according to the equation

$$SOCl_2 + H_2O = SO_2 + 2HCl.$$

**Sulphuryl Chloride, $SO_2Cl_2$,** is formed by the direct action of chlorine upon sulphur dioxide in the sunlight, the action being similar to that which takes place when sulphur dioxide and oxygen unite to form the trioxide:

$$SO_2 + Cl_2 = SO_2Cl_2;$$
$$SO_2 + O = SO_3.$$

It is best prepared by heating the compound $SO_2{<}^{Cl}_{OH}$ to 170°–180°, when the following reaction takes place:

$$2SO_2{<}^{Cl}_{OH} = H_2SO_4 + SO_2Cl_2.$$

It is a liquid which is easily decomposed by water, as represented in the equation

$$SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl.$$

With half the quantity of water required to effect the above decomposition *chlorsulphuric acid*, $SO_2{<}^{Cl}_{OH}$, is formed :

$$SO_2{<}^{Cl}_{Cl} + H_2O = SO_2{<}^{Cl}_{OH} + HCl.$$

**Chlorsulphuric Acid, or Sulphuryl-hydroxyl Chloride,** $SO_2{<}^{Cl}_{OH}$, is also formed, as has been shown, by the direct action of hydrochloric acid upon sulphur trioxide :

$$SO_3 + HCl = SO_2{<}^{Cl}_{OH};$$

and, further, by the action of phosphorus pentachloride upon sulphuric acid :

$$SO_2{<}^{OH}_{OH} + PCl_5 = SO_2{<}^{Cl}_{OH} + POCl_3 + HCl.$$

Like sulphuryl chloride it is decomposed by water, yielding hydrochloric acid and sulphuric acid.

**Compounds of Selenium and Tellurium with Oxygen and with Oxygen and Hydrogen.**—For the purposes of this book it is not necessary to go into details in regard to the compounds of selenium and tellurium. In the introduction to this chapter it was stated that selenium and tellurium form compounds with oxygen corresponding to sulphur dioxide and sulphur trioxide. Both of these oxides of tellurium are known, together with a third of the composition represented by the formula, $TeO$, while only one oxide of selenium, the dioxide, $SeO_2$, is known. On the other hand, the acids of selenium and tellurium, corresponding to sulphurous and sulphuric acids, are known.

**Selenious Acid, $H_2SeO_3$.**—This compound is formed by oxidation of selenium in presence of water or by dissolving selenium dioxide in water. It is a crystallized solid, which attracts moisture from the air, and when heated breaks down into selenium dioxide and water. It forms two series of salts, the acid selenites, $MHSeO_3$, and the nor-

mal selenites, $M_2SeO_3$. While in composition the acid
and its salts are analogous to sulphurous acid and the
sulphites, in conduct there is a marked difference. Sul-
phurous acid tends, as we have seen, to take up more
oxygen and form sulphuric acid, while selenious acid
gives up its oxygen with great ease and yields selenium.
It is evident that the affinity of selenium for oxygen is
much less than that of sulphur for oxygen. When a
solution of selenious acid is treated with sulphur dioxide
the acid is reduced to selenium :

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

The same method of investigation which leads to the
conclusion that sulphurous acid has the formula
$SO_2{<}{H \atop OH}$, when applied to selenious acid, leads to the
conclusion that this has the constitution $SeO{<}{OH \atop OH}$.

Selenic Acid, $H_2SeO_4$, is formed by the action of power-
ful oxidizing agents like saltpeter, or chlorine or bromine
in water solution on selenium. The action with chlorine
is represented thus :

$$Se + 6Cl + 4H_2O = H_2SeO_4 + 6HCl.$$

It is a liquid resembling sulphuric acid. It cannot, how-
ever, be obtained in pure condition on account of its ten-
dency to give up oxygen and pass over into selenious
acid, in which respect it plainly differs markedly from
sulphuric acid. It gives up its oxygen to other substances
much more readily than sulphuric acid does. This is
seen in its action upon hydrochloric acid, which takes
place as represented in the equation

$$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O.$$

Sulphuric acid does not act upon hydrochloric acid,
but it does act upon hydrobromic and hydriodic acids,
and its action upon hydrobromic acid is very similar to

that which takes place between selenic acid and hydro-chloric acid :

$$H_2SO_4 + 2HBr = SO_2 + Br_2 + 2H_2O ;$$

the only essential difference is that the sulphurous acid breaks down into sulphur dioxide and water, while the selenious acid remains in solution as such.

**Selenium Dioxide, $SeO_2$.** — This analogue of sulphur dioxide is made by burning selenium, or by heating selenious acid. It is a solid crystallized substance which can be sublimed without undergoing decomposition and without melting. As we have seen, it dissolves readily in water, forming selenious acid. It loses its oxygen readily in contact with substances which have the power to unite with oxygen, and it is thus reduced to selenium. Hence when it is sublimed particles of dust which may be present in the vessel effect partial reduction, and the product, instead of being white, as the oxide is when pure, is colored by the particles of selenium.

**Acid Chlorides of Selenium.**—Selenium combines with oxygen and chlorine, forming compounds analogous to the acid chlorides of sulphur. The principal one of these is *selenyl chloride*, $SeOCl_2$, which is formed by bringing together selenium tetrachloride and selenium dioxide :

$$SeCl_4 + SeO_2 = 2SeOCl_2.$$

By water it is decomposed, forming selenious and hydro-chloric acids :

$$SeO <^{Cl}_{Cl} + ^{HOH}_{HOH} = SeO <^{OH}_{OH} + 2HCl.$$

Just as sulphur trioxide combines with hydrochloric acid, so also does selenium dioxide. It forms products which are represented by the formulas $SeO_2.2HCl$ and $SeO_2.4HCl$. It is quite possible that the former is a chloride of selenious acid of the constitution $^{Cl}_{Cl} > Se <^{OH}_{OH}$ ,

and that the second should be represented by the formula $\dfrac{H-(Cl_2)}{H-(Cl_2)}{>}Se{<}\dfrac{OH}{OH}$, a few compounds of this kind being known, as will be pointed out.

**Tellurious Acid, $H_2TeO_3$.**—Tellurious acid is formed by treating tellurium tetrachloride with water. It is possible that the first action causes the formation of normal tellurious acid, $Te(OH)_4$, and that this then breaks down into tellurious acid, $H_2TeO_3$, and water:

$$Te\begin{cases} Cl \\ Cl \\ Cl \\ Cl \end{cases} + \begin{array}{l} HOH \\ HOH \\ HOH \\ HOH \end{array} = Te\begin{cases} OH \\ OH \\ OH \\ OH \end{cases} + 4HCl;$$

$$Te\begin{cases} OH \\ OH \\ OH \\ OH \end{cases} = Te\begin{cases} OH \\ OH \\ O \end{cases} + H_2O.$$

The potassium salt of the acid is formed by melting together tellurium dioxide and potassium carbonate:

$$K_2CO_3 + TeO_2 = K_2TeO_3 + CO_2.$$

If the salt thus formed is dissolved in water and nitric acid added to the solution, tellurious acid is thrown down:

$$K_2TeO_3 + 2HNO_3 = 2KNO_3 + H_2TeO_3.$$

It is a solid which easily loses water and is thus transformed into tellurium dioxide.

**Telluric Acid, $H_2TeO_4$.**—This acid is formed by melting tellurious acid with saltpeter and other oxidizing agents. When the solution of the acid is evaporated to crystallization the solid compound deposited has the composition $H_6TeO_6$, and, according to what was learned in studying sulphuric acid, it appears probable that this is normal telluric acid, $Te(OH)_6$. When normal telluric acid is heated to a little above 100° it loses water and is

transformed into the acid $H_2TeO_4$, corresponding to ordinary sulphuric acid, from which most of the tellurates are derived:

$$Te(OH)_6 = TeO_2(OH)_2 + 2H_2O.$$

Heated higher, to about 160°, the acid is decomposed into tellurium trioxide and water:

$$TeO_2(OH)_2 = TeO_3 + H_2O.$$

Although most of the tellurates are simple salts of the acid $H_2TeO_4$, others are derived from more complex forms of the acid. One of these is analogous to disulphuric acid. Another is derived from four molecules of telluric acid, $Te(OH)_6$, by loss of eleven molecules of water.

**Oxides of Tellurium.**— *Tellurium monoxide* is formed by heating sulphur trioxide and tellurium together in a vacuum. *Tellurium dioxide* is formed by burning tellurium or by oxidizing it with nitric acid; and, further, by the decomposition of tellurious acid by heat. It crystallizes and is but slightly soluble in water.

The *trioxide*, $TeO_3$, is formed by heating telluric acid to a high temperature. Its conduct is entirely different from that of sulphur trioxide. While the latter acts with violence upon water, and readily upon metallic oxides and hydrochloric acid, the former does not act readily upon any of these substances. It is insoluble in hot as well as cold water.

**Sulphotelluric Acid** is an example of the sulphur acids referred to on p. 141. While the acid itself is not known, a potassium salt of the formula $K_2TeS_4$ is known. This is plainly analogous to the salt of the oxygen acid, $K_2TeO_4$, differing from it only in containing sulphur in place of the oxygen.

## FAMILY VI, GROUP A.

Group A, Family VI, includes chromium, molybdenum, tungsten, and uranium. All of these show some resemblance to the elements of the sulphur group,

but they also appear in entirely different characters, forming compounds of a kind unknown among the derivatives of sulphur and its analogues. The relation which these elements bear to sulphur is much like the relation which manganese bears to chlorine. The resemblance to sulphur is seen mainly in the formation of acids of the formulas $H_2CrO_4$, $H_2MoO_4$, $H_2WO_4$, and $H_2UO_4$; and the oxides $CrO_3$, $MoO_3$, $WO_3$, and $UO_3$. Most of these acids yield complicated derivatives, all of which can, however, be explained by the same method as that used in the case of periodic acid. The common salts of chromic acid are derived from dichromic acid, which is analogous to disulphuric acid. They have the general formula $M_2Cr_2O_7$. So, too, salts of molybdic acid are known which are derived from the simple form of the acid, $H_2MoO_4$, and others which are derived from a dimolybdic acid, $H_2Mo_2O_7$, and from more complicated forms. Tungsten has a wonderful power of forming complex acids. All of them, however, can be referred to the simple form $H_2WO_4$. And, finally, uranic acid forms salts which for the most part are derived from diuranic acid, $H_2U_2O_7$. All the most important of these compounds will be taken up later.

When the acids of chromium, molybdenum, tungsten, and uranium lose oxygen they form compounds which have little or no acid character. The lower oxides of chromium form salts with acids, and these bear a general resemblance to the salts of aluminium, iron, and manganese. The chromates lose their oxygen quite readily when acids are present with which the chromium can enter into combination in its capacity as a base-forming element. Thus, when potassium chromate $K_2CrO_4$ is treated with hydrochloric acid in the presence of something which can take up oxygen, decomposition takes place thus:

$$2K_2CrO_4 + 10HCl = 4KCl + 2CrCl_3 + 5H_2O + 3O.$$

With sulphuric acid the action takes place as represented in this equation:

$$2K_2CrO_4 + 5H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 3O.$$

In both these cases the chromium enters into combination as a trivalent base-forming element, taking the place of three atoms of hydrogen in hydrochloric acid in the first case, and of three atoms of hydrogen in the sulphuric acid in the second. Molybdenum and tungsten do not form salts of this character; indeed they seem to be practically devoid of basic properties. Uranium, on the other hand, forms some curious salts which differ from the simple metallic salts which we commonly have to deal with. These are the so-called *uranyl* salts, which are regarded as acids in which the hydrogen is either wholly or partly replaced by the group $UO_2$, which is bivalent. Thus, the nitrate has the formula $(UO_2)(NO_3)_2$, the sulphate is $(UO_2)SO_4$, etc. These salts are derived from the compound $UO_2(OH)_2$ acting as a base, whereas this compound has also distinctly acid properties.

# CHAPTER XV.

### NITROGEN, N (At. Wt. 13.93).

**General.**—Nitrogen bears to a group of elements relations very similar to those which oxygen bears to the sulphur group, and fluorine to the chlorine group. There are easily recognized resemblances between it and the members of the group, and yet there are some marked differences. As has been stated, and as is seen from its position in the periodic system, nitrogen is trivalent towards hydrogen, as shown in the compound $NH_3$, while it is both trivalent and quinquivalent towards oxygen, as appears to be shown in $N_2O_3$ and $N_2O_5$. The principal hydrogen compound, ammonia, is entirely different in character from those of chlorine and sulphur, for, while these are acid, ammonia has in a marked way the character of a base, acting, however, in a peculiar way upon acids to form salts. The two oxides above referred to are acidic, forming the acids $HNO_2$ and $HNO_3$, which are known as nitrous and nitric acids respectively.

**Occurrence of Nitrogen.**—It was discovered by Lavoisier and Scheele towards the end of the last century that the air consists of two gases, one of which is oxygen, and they showed that when the oxygen is removed the gas which is left has not the power to support combustion nor to support respiration. This gas was first called *azote* (from $\alpha$, privitive, and ξωτικὸς, life), and this name is still retained in France, the symbol in use in that country being Az, whereas in all others the symbol is N. This is the only case in which there is a difference of usage in respect to the symbols of the chemical elements in different countries. The name *nitrogène* was given to it later, from the fact that it is a constituent of niter or saltpeter, $KNO_3$ (*nitrum*, saltpeter, and γένειν, to pro-

duce), and this is the origin of the English name nitrogen. Not only is nitrogen found free in the air, but it is found in combination in a large number of substances in nature. It is found in the nitrates, or salts of nitric acid, particularly as the potassium salt $KNO_3$, and the sodium salt $NaNO_3$, which occurs in enormous quantities in Chili, and is therefore known as Chili saltpeter. It is also found in the form of ammonia, which is a compound of nitrogen and hydrogen of the formula $NH_3$. Ammonia occurs in small quantity in the air, and is formed under a variety of conditions, to which reference will be made when the substance is treated. Nitrogen occurs, further, in combination in many animal substances.

**Preparation.**—The most convenient way to prepare nitrogen is by burning in a closed vessel something which does not give a gaseous product of combustion; or by passing air over something which has the power to unite with oxygen. The best substance to use for the first purpose is phosphorus, which burns readily and yields a solid product, soluble in water. It is only necessary, therefore, to place a piece of phosphorus in a floating vessel on the surface of water, set fire to it, and immediately place over it a closed bell-jar. As soon as the oxygen is used up the combustion stops, and the vessel then contains the residual nitrogen, and the walls are covered with a thin layer of phosphorus pentoxide, $P_2O_5$. This is soon converted by the water into phosphoric acid, which dissolves. Another convenient method for preparing nitrogen consists in passing air over copper heated in a tube. The copper takes up the oxygen readily, and the nitrogen passes on. Another good method consists in exposing to the air copper turnings partly covered with a solution of ammonia in a vessel so arranged as to allow free access of air while the escape of the gas in the vessel is prevented. This mixture absorbs oxygen slowly at the ordinary temperatures. Nitrogen can also be made from other substances than the air. Thus, when chlorine is passed into a water solution of ammonia this reaction takes place :

$$NH_3 + 3Cl = N + 3HCl;$$

but the hydrochloric acid combines at once with ammonia to form ammonium chloride, $NH_4Cl$:

$$NH_3 + HCl = NH_4Cl;$$

so that the only gaseous product is nitrogen. This experiment is more or less dangerous, for if all the ammonia should be used up, and the passage of chlorine continued, a compound of nitrogen and chlorine which is extremely explosive is formed. Finally, nitrogen can be made by heating ammonium nitrite, $NH_4NO_2$, either dry or in solution. The hydrogen and oxygen of the compound unite to form water and the nitrogen is set free:

$$NH_4NO_2 = 2H_2O + N_2.$$

The nitrogen prepared from the air is never pure, as there are always present in the air other substances besides nitrogen and oxygen; and while some of these can be removed without serious difficulty, others cannot be.

**Properties.**—Nitrogen is a colorless, tasteless, inodorous gas. It has been converted into a liquid by subjecting it to a very low temperature and high pressure. The liquid solidifies at −203°. A liter of nitrogen under standard conditions weighs 1.250 grams. Its specific gravity (air = 1) is 0.971. It does not support combustion, nor does it burn. This latter fact is obvious, for, if nitrogen had the power to combine with oxygen when the temperature of the mixture is elevated, it is plain that this process of combustion would long ago have taken place, leaving one or the other of the two gases and the product of combustion as the constituents of the air. Nitrogen not only does not combine with oxygen readily, but it does not combine readily with any other element except at very high temperature, and then with only a few. Just as it does not support combustion, so also it does not support respiration. Animals would die in it, not on account of any active poisonous properties possessed by it, but for lack of oxygen. In the air it serves the useful purpose of diluting the oxygen. If the air consisted only of oxygen, all processes of combustion would certainly be much more active than they now are. What effect the

continued breathing of oxygen would have upon animals it is impossible to say.

**The Air.**—The atmosphere of the earth, commonly called the air, consists essentially of the two elements nitrogen and oxygen in the proportion of 79 volumes of nitrogen to 21 volumes of oxygen, or, by weight, of 77 per cent of nitrogen and 23 per cent of oxygen. Wherever air has been collected and analyzed it has been found to have practically the same composition. Nevertheless very accurate analyses have shown that the composition of the air is subject to slight variations. To decide whether the air is a chemical compound or a mechanical mixture requires a careful examination of a number of facts. The evidence may be summed up as follows :

(1) If nitrogen and oxygen are mixed together the mixture conducts itself in exactly the same way as air. The mixing is not attended by any phenomena indicating chemical action. Generally the chemical combination of two elements is accompanied by an evolution of heat, and whenever a chemical act takes place there is some change in the temperature of the substances. When nitrogen and oxygen are brought together there is no change in the temperature of the gases.

(2) The composition of a chemical compound is constant. The law of definite proportions is founded upon a very large number of observations, and in all cases in which we have independent evidence that chemical action takes place it is found that the substances combine in exactly the same proportions to form the same product. Variation in the composition of a chemical compound is not known. The composition of the air varies slightly, according to circumstances, and this fact may be regarded as evidence that the air is not a chemical compound.

(3) Air dissolves somewhat in water. If air which is in solution in water is pumped out and analyzed, it is found to have a different composition from that of ordinary air. Instead of containing nearly 4 volumes of nitrogen to 1 of oxygen, it contains only 1.87 volumes of nitrogen to 1 of oxygen. The proportion of oxygen is

much larger in the air which has been dissolved in water than it is in ordinary air. This is due to the fact that oxygen is more soluble in water than nitrogen. Therefore, when air is shaken with water, relatively more oxygen than nitrogen is dissolved. If the gases were in chemical combination we should expect the compound to dissolve as such and without change of composition.

The above evidence shows that nitrogen and oxygen are not combined chemically in the air, but that they are simply mixed together.

As enormous quantities of oxygen are constantly employed in the processes of respiration of animals, combustion, and various kinds of decay, the question will suggest itself : Is the quantity of oxygen in the air decreasing ? In regard to this point some ingenious calculations have been made the results of which are reassuring. An approximate estimate of the extent of the atmosphere, and therefore of the supply of oxygen, can easily be made. Assuming that the population of the earth is 1000 million human beings, the quantity of oxygen used by them in respiration in a year would amount only to about $\frac{1}{3800000}$ part of the supply. Suppose, further, that for all other purposes nine times as much oxygen is required as for the respiration of human beings, then the total amount used up in a year would be only $\frac{1}{380000}$ of the whole supply. In 3800 years the decrease in the amount of oxygen in the air would be only 1 per cent. Whether there has been such a decrease or not it is impossible to say, as it is only within a comparatively few years that accurate analyses have been made. It appears probable, however, from other considerations that the quantity of oxygen in the air is not decreasing. It is known that the process of plant life involves a giving off of oxygen which comes from other compounds. The plants have the power to decompose the carbon dioxide found in the air, and they utilize the carbon and a part of the oxygen, but another part they give back to the air, so that in the process of vegetable growth we have a constant source of supply of oxygen.

**Analysis of Air.**—The earliest examinations of Priest‑ley, Lavoisier, and Scheele were made by burning sub‑stances in air contained in closed vessels. They con‑cluded that the air is made up of $\frac{1}{5}$ oxygen and $\frac{4}{5}$ nitrogen by bulk. In order to determine the composition of the air to-day, we should proceed as follows: A qualitative examination would easily show the presence of nitrogen and oxygen. If a solution of calcium hydroxide, $Ca(OH)_2$, which is known as lime-water, or a solution of barium hydroxide, $Ba(OH)_2$, is exposed to the air it becomes turbid, and a precipitate is formed. Neither nitrogen nor oxygen nor an artificially prepared mixture of the two gases can produce this change. It has been shown that the change is due to the presence in the air of a small quantity of the gaseous compound, carbon dioxide, $CO_2$. If calcium chloride or phosphorus pentoxide is exposed to the air it soon becomes moist and after a time turns liquid. This effect has been found to be due to the pres‑ence of water vapor in the air. Nitrogen obtained from the air by passing the latter over copper, which abstracts the oxygen, has been shown to contain a small amount of an extremely inert gas, argon (which see). By other methods which need not be considered here it can be shown that there are many other substances in the air besides those mentioned. Among them are ammonia, hydrogen dioxide, and organic matters of various kinds, including a large variety of germs the presence of which can be detected by the changes which exposure to the air produces in certain liquids, as milk and fruit juices.

Having thus learned what the chief constituents of the air are, the next thing is to determine in what quantities they are present, or to make a *quantitative analysis* of the air. For this purpose advantage may be taken of the fact that phosphorus when exposed to the air at ordinary temperatures combines slowly with the oxygen, leaving the nitrogen. If, therefore, a piece of ordinary phosphorus is inserted into a measured volume of air contained in a graduated glass tube over water or mer‑cury, a diminution in volume will take place slowly. If,

in the course of a few hours, the volume is again measured, the difference will give the volume of oxygen absorbed, while the gas remaining is nitrogen. Of course, in this case as in all others in which gas volumes are measured, corrections for temperature, pressure, and tension of aqueous vapor must be made.

Another method by which the ratio between the nitrogen and oxygen in air can be determined is that which was first employed by Dumas and Boussingault. It consists in passing air over heated copper, collecting and measuring the nitrogen, and weighing the copper oxide. The apparatus is arranged as shown in Fig. 9.
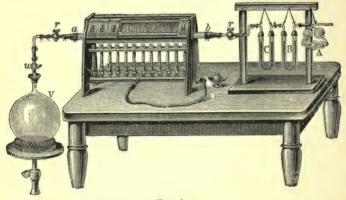


Fig. 9.

The copper is contained in the glass tube *ab* on the combustion furnace. At the ends of this tube are the stop-cocks *rr*. *V* is a glass globe provided with a stop-cock *u*. Before the experiment the air is exhausted from the globe and the tube *ab*, and the tube then carefully weighed. The tubes *B* and *C* and the apparatus *A* contain substances which have the power to absorb the carbon dioxide of the air. The tube *ab* is now heated and air admitted after passing through *C*, *B*, and *A*. The copper takes up the oxygen, and the nitrogen enters the globe *V*. After the globe is full it is weighed, then exhausted and weighed again, and the difference gives the weight of the nitrogen. The tube is also exhausted and weighed, and the difference between this weight and that

of the exhausted tube before the experiment gives the weight of the oxygen.

The most refined method for the analysis of the air is the eudiometric method of Bunsen. This consists in adding some pure hydrogen to a measured volume of air contained in a eudiometer over mercury, and then exploding the mixture by means of an electric spark. If the conditions are right all the oxygen present will combine with hydrogen, and in consequence of this there will be a corresponding contraction in the volume of the gases. The amount of contraction will be equal to the volume of hydrogen and that of oxygen which have combined to form water. But we know from previous experiments on these two gases that they combine in the ratio of one volume of oxygen to two of hydrogen. Consequently the volume of oxygen which was present is equal to one third of the total contraction. Of course it is necessary that there should be enough hydrogen present to combine with all the oxygen. This method is capable of great exactness. The most accurate analyses made by this method by Bunsen and others have shown that in 100 volumes of air there are 20.9 to 21 volumes of oxygen.

The estimation of the quantity of water vapor present in the air is an important problem. The quantity present depends upon a variety of causes, the temperature and the direction of the wind being the chief ones. A good chemical method for estimating the water consists in drawing a known volume of air over calcium chloride in a weighed tube. This substance has the power to take up water, as we have repeatedly seen. If the tube is weighed after a certain volume of air has been drawn through it, the increase in weight will show the weight of water contained in that volume of air.

The quantity of water vapor present in the air varies between comparatively wide limits. At any given temperature the air cannot hold more than a certain quantity. When it contains this quantity it is said to be *saturated*. If cooled down below this temperature the vapor partly condenses, and appears now as water. When a vessel containing ice is placed in the air, that which immedi-

ately surrounds the vessel is cooled down below the point at which the quantity of water vapor present would saturate the air, and water condenses on the outside of the vessel. Every one has noticed that on a warm cloudy day more water condenses on such a vessel than on a clear cool day. The water vapor present in the air has an important effect on man. The inhabitants of countries with moist climates apparently have characteristics which are not generally met with in those who inhabit countries with dry climates. The difference in the effects of moist and of dry air on an individual is well known.

When air which is charged with water vapor comes in contact with cooler air, the vapor condenses and falls as rain.

The method employed for the purpose of estimating the quantity of carbon dioxide in the air consists in drawing a known volume of air over something which has the power to absorb the carbon dioxide, and then determining the increase in weight of the absorbing substance. Potassium or sodium hydroxide is well adapted to this. An apparatus has been constructed in which barium hydroxide, $Ba(OH)_2$, is used as the absorbent. When carbon dioxide is passed through a solution of this substance insoluble barium carbonate, $BaCO_3$, is thrown down according to the equation

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

This may be filtered off and weighed, and the quantity of carbon dioxide estimated from the results; or, if a known quantity of the hydroxide is taken, the quantity left unacted upon after the experiment can be determined by neutralizing with an acid, the neutralizing power of which has previously been determined with care. The quantity of carbon dioxide present in the air is relatively very small, being about 3 parts in 10,000. It varies slightly according to the locality and season, being greater in cities and in summer than in the country and in winter; and greater in warm countries than in cold. It is as essential to the life of plants as oxygen is to the life of animals.

It is not an easy matter to determine the quantities of the other constituents of the air, as the ammonia, organic substances, etc., though there is no difficulty in determining that they are present in very small quantities.

The relations of the air to the most important chemical changes which are taking place upon the earth form one of the most interesting subjects for all men. We have had a slight glimpse of the action of oxygen, and of that of carbon dioxide ; both are essential to the life of plants and animals. So, too, the water vapor acts chemically upon plants, and probably to some extent in the respiration of animals. As regards the nitrogen, this element is frequently referred to as inert, and as serving the purpose of diluting the oxygen. Inert it undoubtedly is, and there is also no doubt that it dilutes the oxygen, but these statements give a very inadequate conception of the important part played by it in the processes of nature. Nitrogen in some form of combination is an essential constituent of plants and animals. The animals get their nitrogenous compounds from the plants, and the plants get theirs partly at least from the soil. By the growth of plants, therefore, nitrogenous compounds are constantly being withdrawn from the soil. When plants and animals undergo decomposition in the soil, the nitrogen contained in them is gradually converted into salts of nitric acid or nitrates, and if the decomposition takes place in the air the nitrogen is converted principally into ammonia. Both in the form of nitrates and of ammonia the nitrogen can be utilized by plants, so that if the plants and animals which have received their nourishment from a certain tract of land should be allowed to decay upon this land after death, and the products thus formed should be uniformly distributed in the soil, the latter would not become exhausted. But the products of the soil are removed, and, therefore, the nitrogen required for the growth of other plants is removed, and the soil becomes unproductive. In order that it may be rendered fertile again, the lost nitrogen must be supplied. It appears from recent very elaborate experiments that the plants have the power to take up from

the air a part of the nitrogen which they need. Whether they take it up directly, or it is first taken up by the soil and converted into some compound which the plants can utilize, are questions which apparently have not been answered satisfactorily as yet. It appears possible, further, that in this absorption of nitrogen from the air certain minute organisms which exist in the soil play a part.

Pure air may be defined as air which consists of nitrogen, oxygen, and carbon dioxide in the proportions stated above, together with some water vapor, ammonia, hydrogen dioxide, and argon, and nothing of an injurious nature. It is evident from what has been said that there is constant danger of contamination from natural causes. The most common cause of contamination is the breathing of human beings in rooms which are inadequately supplied with air. The breathing process involves the using up of oxygen and the giving off of carbon dioxide and small quantities of organic matter which is undergoing decomposition. If the quantity of oxygen is reduced below a certain limit the air becomes unfit for breathing purposes, and evil effects follow. An ordinary inhalation will not then be sufficient to supply the blood with the oxygen necessary to purify it, and the system will begin to suffer. Headache, drowsiness, and a general sense of discomfort follow. The ill effects of breathing the air of a badly ventilated room occupied by a number of human beings appear to be due for the most part to the presence of the small quantities of decomposing organic matters which are given off from the lungs with the carbon dioxide and other gases. These act as poisons. They have been thrown off from the lungs because they are unfit for use, and when they are taken back again the normal processes of the body are interfered with. The subject of ventilation has been so thoroughly discussed of late years that great improvement has been made in the arrangements for supplying pure air to dwelling apartments and audience halls, but there is still room for improvement. Fortunately, in most buildings there is one source of supply of pure air which is independent of

architects' plans. This is the diffusion of gases through the porous materials of which the buildings are constructed. This diffusion was referred to under the head of Hydrogen (see p. 45). There is also a good deal of ventilation through the cracks and other apertures which are always to be found in our buildings.

Under some conditions not thoroughly understood the air becomes contaminated by the decomposition of animal and vegetable matter. Air thus contaminated may cause specific diseases, and some of these are spoken of as being caused by *malaria*, a word which signifies simply bad air. It has been shown that there are in the air microscopic germs which have the power to develop in the body, and then to cause the symptoms which are referred to malaria. Disease germs and germs of other kinds are present in the air in great variety, and they play an important part in connection with the life and health of mankind.

**Argon.**—Lord Rayleigh has shown that a liter of nitrogen prepared from the air by abstracting the oxygen and the small quantities of other substances known to be present weighs 1.2572 grams, while a litre of nitrogen made from some chemical compound, such as ammonia, weighs 1.2505 grams. Chemically prepared nitrogen is lighter than that obtained from the air. This observation led Lord Rayleigh and W. Ramsay to a more thorough chemical examination of the air, the result of which was the discovery of a constituent previously unknown. This is the gas argon. It can be obtained by either of two methods: (1) By passing air over heated copper until all the oxygen is abstracted, and then over heated magnesium which unites with the nitrogen but leaves the argon; (2) By mixing air with oxygen and passing electric sparks through the mixture. The oxygen and nitrogen combine and the product can easily be removed. After all the nitrogen has thus been removed argon remains behind. Argon is an element with the atomic weight about 40. It is present in the air to the extent of about 1 per cent of the nitrogen. It cannot be made to combine with any other element.

# CHAPTER XVI.

## COMPOUNDS OF NITROGEN WITH HYDROGEN—WITH HYDROGEN AND OXYGEN—WITH OXYGEN, ETC.

**General Conditions which give Rise to the Formation of the Simpler Compounds of Nitrogen.**—We have seen that nitrogen is an inactive element, showing little tendency to combine with other elements. It is nevertheless an easy matter to get compounds of nitrogen with many other elements, and among these compounds, some of those which it forms with hydrogen and oxygen are of much importance.

When a compound which contains carbon, hydrogen, and nitrogen, and is not volatile, is heated in a closed vessel, so that the air does not have access to it, the nitrogen passes out of the compound, not as nitrogen, but partly in combination with hydrogen, in the form of the compound *ammonia*. Nearly all animal substances contain carbon, hydrogen, oxygen, and nitrogen in many forms of combination, some of which are quite complicated. Many of these give off ammonia when heated. Similarly, compounds containing carbon, oxygen, and hydrogen, even though they are thoroughly dry, when heated give off oxygen in combination with hydrogen in the form of water. Both these kinds of decomposition, that which gives ammonia and that which gives water, are to be ascribed to the fact that the compounds of carbon which are heated are unstable at higher temperatures, and when they are broken down the elements contained in them arrange themselves in combination in stable forms, such as the comparatively simple compounds, water and ammonia. An illustration of this kind of action was referred to in speaking of the preparation of nitrogen by heating ammonium nitrite. This compound

breaks down very easily under the influence of heat, the hydrogen and oxygen combining to form the stable compound water, while the nitrogen remains uncombined. Some animal substances, as, for example, urine, give off ammonia when they undergo spontaneous decomposition in the air. This decomposition is generally, if not always, due to the action of minute organisms, the germs of which are in the air, which develop when they come in contact with certain substances. The coal which is used for making illuminating gas contains some hydrogen and nitrogen in chemical combination, and when the coal is heated ammonia is given off with the other products.

When animal substances undergo decomposition in the presence of basic compounds where the temperature is comparatively high, the nitrogen combines with oxygen and with the metal of the base. Either a salt of nitric acid, $HNO_3$, or of nitrous acid, $HNO_2$, is formed. In some countries where the conditions are favorable to the process, immense quantities of nitrates are found, chiefly potassium nitrate, $KNO_3$, and sodium nitrate, $NaNO_3$. Nitrates are, however, found everywhere in the soil. The change of animal and vegetable nitrogenous substances to the form of nitrates is probably caused by the action of minute living organisms, which are found everywhere, and serve an important purpose in converting the waste animal and vegetable matter into simple compounds which can be utilized by plants. How they effect the change is not known. From the salts of nitric acid which are found in nature, nitric acid itself can easily be made.

Nearly all the compounds of nitrogen with which we have to deal are made either from ammonia or from nitric acid.

**Relations between the Principal Compounds of Nitrogen.**—In studying the compounds of sulphur, we saw that whenever a compound of sulphur is oxidized with a strong oxidizing agent the final product of the action is sulphuric acid; and that, on the other hand, under the influence of strong reducing agents these compounds yield hydrogen sulphide as the final product. So also

the limit of oxidizing action in the case of chlorine is perchloric acid, and of reducing action, hydrochloric acid. The other compounds of sulphur with hydrogen and oxygen are products intermediate between the two limits, sulphuric acid and hydrogen sulphide, as the other compounds of chlorine with hydrogen and oxygen are intermediate between hydrochloric acid and perchloric acid. The limit of reduction of nitrogen compounds is ammonia, $NH_3$, and of oxidation, nitric acid, $HNO_3$. As has been noticed, the valence of nitrogen towards oxygen is greater than it is towards hydrogen, but the difference is not as marked as in the case of the members of the chlorine group, and in that of the sulphur group. Its hydrogen valence is 3, its maximum oxygen valence is 5. For reasons similar to those which have already been discussed under the head of Hydroxides, the oxidation products of ammonia are believed to have their oxygen in combination with hydrogen in the form of hydroxyl, so far as these two elements are present in the right proportions to form this group. If this is true the first product of oxidation of ammonia would have the structure represented by the formula

$$N \begin{cases} OH \\ H \\ H \end{cases}$$ . A compound of the composition represented by

$NH_3O$ is known, and it is believed that it has the above structure. The next product of oxidation formed by the

same process would have the formula $N \begin{cases} OH \\ OH \\ H \end{cases}$. No such

compound is known, however. If a compound of this structure should lose water the product would have the composition $NOH$, and probably the structure $O=N-H$. A compound of the composition represented by this formula is known, but it seems probable from its conduct that the formula should be doubled, $N_2O_2H_2$, and that in the compound there are two hydroxyl groups, as

represented in the formula $\begin{matrix} N-OH \\ \| \\ N-OH \end{matrix}$. Continuing the pro-

cess of oxidation of ammonia, the next product which

we should expect would be the trihydroxyl derivative

$N \begin{cases} OH \\ OH \\ OH \end{cases}$. Salts derived from an acid of this composition,

which should be called *normal nitrous acid*, are known.
But this normal acid breaks down readily by loss of water

into an acid of the formula $N \begin{cases} O \\ OH \end{cases}$ or $O{=}N{-}O{-}H$,

which is the acid from which nearly all the nitrites are
derived. By continued oxidation the quinquivalence of
the nitrogen makes it possible to add another oxygen
atom to the molecule of nitrous acid, and thus to form
the final product of oxidation, nitric acid of the structure

$\overset{O}{\underset{O}{\overset{\|}{N}}}{-}O{-}H$; or, if the oxidation takes place in solution, it

is probable that the final product is a hydroxyl deriva-

tive of the structure $N \begin{cases} OH \\ OH \\ OH \\ OH \\ OH \end{cases}$, which should be called

*normal nitric acid.* There are some salts known which
are derived from an acid of this composition, but most
of the nitrates are derived from an acid which is formed
from this by loss of two molecules of water:

$$N(OH)_5 = NO_2(OH) + 2H_2O.$$

It is impossible at present to furnish satisfactory evi-
dence in favor of the views just pointed out. All that
can be said is that the views are in accordance with a
number of facts, and that they simplify the study of the
relations of the compounds.

When nitric acid is reduced, of course, the above pro-
cesses must be regarded as reversed. Thus, the first
result of the action of nascent hydrogen upon nitric acid,
for example, would be the elimination of one atom of
oxygen and the formation of nitrous acid:

$$NO_2(OH) + 2H = NO(OH) + H_2O.$$

The next result would be the formation of the compound $N(OH)$ or $N_2O_2H_2$; the next the formation of the compound $NH_2(OH)$; and finally this would be converted into ammonia. But the matter is complicated by the fact that some of the compounds referred to above break down into water and oxides of nitrogen. Thus, nitrous acid, $NO(OH)$, breaks down into water and nitrogen trioxide or nitrous anhydride, $N_2O_3$; and the compound $N_2O_2H_2$, or hyponitrous acid, breaks down into water and nitrous oxide, $N_2O$:

$$2N \begin{Bmatrix} OH \\ O \end{Bmatrix} = N_2O_3 + H_2O \, ;$$

$$\begin{array}{c} N(OH) \\ \| \\ N(OH) \end{array} = N_2O \; + H_2O.$$

Further, there are some compounds of nitrogen and oxygen for which there are no analogous hydroxyl compounds known, as, for example, $NO$ and $NO_2$ or $N_2O_4$. In these compounds nitrogen appears to be bivalent and quadrivalent, while in nitrous oxide, $N_2O$, it appears to be univalent. Only those oxygen compounds of nitrogen in which the nitrogen is univalent, trivalent, or quinquivalent appear to form corresponding hydroxyl compounds. Taking the simplest view of the matter, nitrogen appears to be univalent, bivalent, trivalent, quadrivalent, and quinquivalent towards oxygen, as shown in the compounds

$$N_2O, \quad NO, \quad N_2O_3, \quad NO_2, \quad \text{and} \quad N_2O_5.$$

Corresponding to nitrous oxide, $N_2O$, nitrogen trioxide, $N_2O_3$, and nitrogen pentoxide, $N_2O_5$, there are hydroxyl derivatives which have acid properties:

$$N_2O \; + H_2O = N_2(OH)_2 \, ;$$
$$N_2O_3 + H_2O = 2NO(OH) \, ;$$
$$N_2O_5 + H_2O = 2NO_2(OH).$$

But there are no hydroxyl derivatives corresponding to those oxides in which the valence appears to be 2 and 4. Considering the ease with which those hydrox-

ides of nitrogen break down which contain two hydroxyl groups in the molecule, the fact that hydroxides of the formulas $N(OH)_2$ and $N(OH)_4$ do not exist is not surprising. We should expect them to break down spontaneously into NO and $NO_2$.

The methods by which it is possible to pass from one of the oxides or hydroxides of nitrogen to the other will be pointed out below. A tabular list of the compounds is first given:

| *Oxides.* | *Acids.* |
|---|---|
| Nitrous oxide, $N_2O$ | Hyponitrous acid, $N_2(OH)_2$ |
| Nitric oxide, $NO(N_2O_2)$ | Nitrous acid, $NO(OH)$ |
| Nitrogen trioxide, (Nitrous anhydride), } $N_2O_3$ | Nitric acid, $NO_2(OH)$ |
| Nitrogen peroxide, $NO_2(N_2O_4)$ | |
| Nitrogen pentoxide, (Nitric anhydride), } $N_2O_5$ | |

Besides the above there are the basic compounds, *hydroxylamine*, $NH_2(OH)$, *ammonia*, $NH_3$, and *hydrazine*, $N_2H_4$; and with water ammonia probably forms the hydroxide $NH_4(OH)$, which is a base. In addition to these there is a compound of nitrogen with hydrogen of the formula $N_3H$. This is a strong acid. (See Triazoic Acid.) And of the same composition as hyponitrous acid but differing from it in properties is *nitramide*, $N_2H_2O_2$, the relation of which to hyponitrous acid is not yet quite clear.

With the members of the chlorine group nitrogen forms a few compounds which are characterized by marked instability. So unstable are they that they explode violently when simply touched. The chloride of nitrogen explodes with terrific violence when the direct rays of the sun are allowed to shine upon it. With sulphur, nitrogen forms two compounds. With sulphur, hydrogen, and oxygen, however, nitrogen forms a number of compounds, one of which has already been referred to in connection with the manufacture of sulphuric acid. This is the so-called nitrosyl-sulphuric acid which is formed by the action of a mixture of the peroxide, $NO_2$,

and the monoxide, NO, on sulphurous acid, oxygen, and water.

In studying the compounds of nitrogen, it will be best to begin with the end products, ammonia and nitric acid.

**Ammonia, NH₃.**—The conditions under which ammonia is formed have been mentioned. The chief source at present is the "ammoniacal liquor" of the gas-works. This is the water through which the gas has been passed for the purpose of removing the ammonia, and it contains ammonia, or ammonium hydroxide, $NH_4(OH)$, in solution. By adding hydrochloric acid to this solution the salt *ammonium chloride*, $NH_4Cl$, is formed. This is the well-known substance *sal ammoniac*. It appears that this name has its origin in the fact that common salt or sodium chloride, NaCl, was formerly called *sal armeniacum*, and that afterward, through a misunderstanding, ammonium chloride came to be known by the same name which underwent change to the form *sal ammoniacum*, or *sal ammoniac*. When the ammoniacal liquor is treated with sulphuric acid, ammonium sulphate is formed. From one or the other of these salts it is a simple matter to obtain ammonia. For this purpose it is only necessary to treat the salt with some strongly basic compound, as, for example, potassium or sodium hydroxide, or calcium hydroxide. Thus, when a solution of potassium hydroxide is poured on ammonium chloride or sulphate the strong penetrating odor of ammonia is at once noticed. The first reaction probably results in the formation of ammonium hydroxide, thus :

$$NH_4Cl \quad + KOH \quad = NH_4OH + KCl;$$
$$(NH_4)_2SO_4 + 2KOH \quad = 2NH_4OH + K_2SO_4;$$
$$2NH_4Cl \quad + Ca(OH)_2 = 2NH_4OH + CaCl_2;$$
$$(NH_4)_2SO_4 + Ca(OH)_2 = 2NH_4OH + CaSO_4.$$

But the ammonium hydroxide breaks down very readily into water and ammonia, which escapes as a gas :

$$NH_4OH = NH_3 + H_2O.$$

Further, ammonia can also be made by bringing

nascent nitrogen and nascent hydrogen together, as, for example, by heating a mixture of iron filings, potassium nitrate, and potassium hydroxide. Under these circumstances the iron sets hydrogen free from the hydroxide, and nitrogen from the nitrate, and they unite to form ammonia. The formation of ammonia by reduction of nitric acid can be shown by treating some granulated zinc with dilute sulphuric acid, and while the action is in progress adding nitric acid drop by drop. The nitric acid is thus reduced, and the ammonia which is formed remains in combination with the sulphuric acid as ammonium sulphate. Other interesting modes of formation of ammonia are by the action of electric sparks on nitrogen in the presence of water, and, in general, by the evaporation of water :

$$N_2 + 2H_2O = NH_4NO_2.$$

The product *ammonium nitrite* is always found in the air in small quantities.

In the laboratory ammonia is prepared by treating ammonium chloride with slaked lime or calcium hydroxide. The two are mixed in the proportion of two parts of slaked lime to one of ammonium chloride, placed in a flask and gently heated, when the ammonia is given off at once.

It is frequently more convenient to heat a strong aqueous solution of ammonia, such as is found in every chemical laboratory. Such a solution when gently heated readily gives off ammonia.

Ammonia is a colorless, transparent gas with a very penetrating, characteristic odor. In concentrated form it causes suffocation. Its specific gravity is 0.589; that is to say, it is but little more than half as heavy as air. A liter of the gas under standard conditions weighs 0.7635 gram. It can easily be compressed to the liquid form by pressure and cold. When the pressure is removed from the liquefied ammonia it passes back to the form of gas, and in so doing it absorbs a great deal of heat. These facts are taken advantage of for the arti-

ficial preparation of ice. This application will be clear
from the following explanation and Fig. 10.

An aqueous solution of ammonia saturated at 0° is
brought into the strong iron cylinder *A*, and then gently
warmed, while the vessel *B* is cooled by cold water.
The gas given off from *A* passes though the bent tubes
into *B*, where it is condensed
to a liquid. The cylinder
*A* is now placed in a ves-
sel of cold water, and the
water which is to be frozen is
placed in a cylinder *D*, and
this into the hollow space *E*
in the vessel *B*. The liquid
ammonia passes rapidly into
the form of gas which is ab-
sorbed in the water in *A*,
while at the same time so
much heat is absorbed that the water in *D* is frozen.
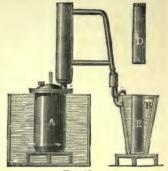


Fig. 10.

Ammonia does not burn in the air, but does burn in
oxygen with a pale yellowish flame. It is absorbed by
water in very large quantity. One volume of water at
the ordinary temperature dissolves about 600 volumes of
ammonia gas, and at 0° about 1000 volumes. The sub-
stance with which we commonly have to deal under the
name of ammonia is a solution of ammonia in water. It
is called "spirits of hartshorn" in common language. The
solution has the odor of the gas. It loses all its gas when
heated to the boiling temperature. The solution shows
a strong alkaline reaction, and has the power to neutral-
ize acids and form salts. The conduct of the solution is,
in fact, strikingly like that of sodium and potassium
hydroxides, and it is believed that in the solution there
is contained a compound of the formula $NH_4(OH)$, known
as ammonium hydroxide, and formed by the direct action
of ammonia upon water. If this is true, then the action
of ammonia upon acids is to be explained as follows:
Ammonium hydroxide is analogous to potassium hydrox-
ide, but differs from it in that it contains the group of
atoms $NH_4$ in place of the atom K. In some way this

group plays in the salts formed by ammonia the same part that the elementary atom potassium plays in the salts of potassium, and just as the latter are called potassium salts, so the former are called *ammonium salts*. According to this the ammonium salts are salts which contain the group $NH_4$, known as the ammonium group, in place of the hydrogen of the acids. They are formed by direct combination of ammonia with the acids, or by the action of ammonium hydroxide upon acids. The analogy between the action of ammonium hydroxide and that of potassium hydroxide upon acids is clearly shown by the aid of the following equations:

$$K(OH) \quad + HCl \quad = KCl \quad\quad + H_2O;$$
$$NH_4(OH) + HCl \quad = NH_4Cl \quad + H_2O;$$
$$K(OH) \quad + HNO_3 = KNO_3 \quad + H_2O;$$
$$NH_4(OH) + HNO_3 = NH_4NO_3 + H_2O;$$
$$2K(OH) \quad + H_2SO_4 = K_2SO_4 \quad + 2H_2O;$$
$$2NH_4(OH) + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

The formation of the ammonium salts by direct action of ammonia, $NH_3$, upon acids is represented in the following equations:

$$NH_3 \quad + HCl \quad = NH_4Cl;$$
$$NH_3 \quad + HNO_3 = NH_4NO_3;$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The strong tendency of ammonia to combine directly with acids is shown by bringing two uncovered vessels, one containing a solution of ammonia, and the other a solution of hydrochloric acid, near each other. A dense cloud will at once be noticed, if the solutions are concentrated. This is due to the direct combination of the gases which escape from the solutions.

While the assumption of the existence of the group ammonium, $NH_4$, in the ammonium salts is of great service in dealing with these salts, and while this assumption appears to be entirely justified by the facts, no compound of this composition has as yet been isolated.

The name ammonium is given to the hypothetical compound on account of the fact that it evidently plays the part of a metallic element, and it is customary to give such elements names ending in *ium*. While, further, it is generally believed that the compound ammonium hydroxide, $NH_4(OH)$, is formed when ammonia dissolves in water, the compound itself has not been isolated, owing to its instability and tendency to break down into ammonia and water. On the other hand, some very interesting derivatives of this hydroxide have been isolated. There is one of these which is derived from the hydroxide by the replacement of the four hydrogen atoms of the ammonium by groups of carbon and hydrogen atoms. This compound is stable and can be isolated as a hydroxide of the general formula $NR_4(OH)$, in which $R_4$ represents the groups of carbon and hydrogen atoms. It acts almost exactly like potassium hydroxide.

**Composition of Ammonia.** — By oxidation under the proper conditions it is possible to convert the hydrogen of ammonia into water and leave the nitrogen in the free state. As water and nitrogen are the only products formed, and the quantity of oxygen used up in the oxidation is equal to the quantity of oxygen found in the water formed, it follows that nitrogen and hydrogen are the only elements contained in ammonia.

When electric sparks are passed for some time through a mixture of nitrogen and hydrogen, some ammonia is formed. Conversely, when electric sparks are passed for a time through ammonia, nitrogen and hydrogen are obtained.

If, in the oxidation of a known weight of ammonia, the water formed and the nitrogen left uncombined are accurately determined, it will be found that in ammonia the elements are combined very nearly in the proportion of *fourteen parts by weight of nitrogen to three parts by weight of hydrogen*. Further, the molecular weight determined by the method of Avogadro is approximately 17. Therefore, the molecular formula of ammonia is $NH_3$, the atomic weight of nitrogen being 14.

The proportion by volume in which the two elements

combine can be determined by the following method: A glass tube closed at one end and provided with a glass stop-cock at the other is filled with pure chlorine gas. By means of a small funnel attached to the open end a little of a strong aqueous solution of ammonia is slowly introduced into the tube. Reaction takes place at once between the chlorine and the ammonia, according to the equation

$$NH_3 + 3Cl = N + 3HCl;$$

and the hydrochloric acid unites with ammonia to form ammonium chloride:

$$3HCl + 3NH_3 = 3NH_4Cl.$$
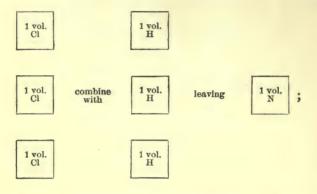
The entire change is therefore represented by the equation

$$4NH_3 + 3Cl = N + 3NH_4Cl.$$
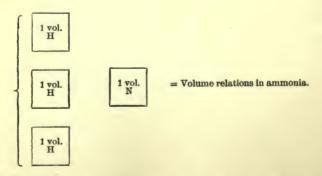
Hydrogen and chlorine combine in equal volumes, as we have already learned. Now, if we start with a measured volume of chlorine, and add ammonia to it until it is all used up, we know that the volume of hydrogen which has been extracted from ammonia is equal to the volume of chlorine with which we started. If we measure the volume of nitrogen left over, we know the volume of the nitrogen which was in combination with a volume of hydrogen equal to that of the chlorine originally taken. This experiment has been tried repeatedly, and it has been found that the ratio of the volume of nitrogen to that of the hydrogen with which it was combined is as 1 to 3. The tube being full of chlorine at the beginning of the experiment, it will be found to be one-third full of nitrogen at the end. *Therefore, in ammonia 1 volume of nitrogen is combined with 3 volumes of hydrogen.*

The experiment just referred to will perhaps be better

understood by the aid of the accompanying diagram.
The chlorine in the tube may be represented as made
up of three equal parts or volumes. Each volume of
chlorine combines with an equal volume of hydrogen,
leaving the nitrogen uncombined. The volume of nitro-
gen left is only one third of that of the chlorine, or for
three volumes of chlorine there is one volume of nitrogen:

| 1 vol. Cl | | 1 vol. H | | |
|-----------|---|----------|---|---|
| 1 vol. Cl | combine with | 1 vol. H | leaving | 1 vol. N ; |
| 1 vol. Cl | | 1 vol. H | | |

Therefore in ammonia the gases nitrogen and hydrogen
are combined in the proportion of 1 volume of nitrogen
to 3 volumes of hydrogen:

| 1 vol. H | | |
|----------|---|---|
| 1 vol. H | 1 vol. N | = Volume relations in ammonia. |
| 1 vol. H | | |

Another question in regard to the volume relations
remains to be answered, and that is: When nitrogen and
hydrogen unite in the proportions above stated, how
many volumes of ammonia gas do the four volumes of

the constituents form? It is not possible to determine this by direct combination of the two gases, but ammonia can be decomposed into its constituents by continued passage of electric sparks through it. When this is done it is found that after the decomposition the gases occupy twice the volume which was occupied by the ammonia. It appears, therefore, that when hydrogen and nitrogen combine to form ammonia the volume is reduced to one half, or, what is the same thing, when three volumes of hydrogen combine with one volume of nitrogen the four volumes form two volumes of ammonia gas.

The above facts have already been commented upon in speaking of the combination of gases in general; and it has been shown that chlorine, oxygen, and nitrogen combine with hydrogen in entirely different ways:

(1) 1 volume of chlorine combines with 1 volume of hydrogen to form 2 volumes of hydrochloric acid gas.

(2) 1 volume of oxygen combines with 2 volumes of hydrogen to form 2 volumes of water vapor.

(3) 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia gas.

What the cause of these differences is we do not know. In some way these facts are directly connected with the law of Avogadro that equal volumes of all gases contain the same number of molecules, and with the power of the atoms of chlorine, oxygen, and nitrogen to combine with one, two, and three atoms of hydrogen respectively. When one atom of chlorine unites with one atom of hydrogen the result is a molecule. So also when one atom of oxygen unites with two atoms of hydrogen, and when one atom of nitrogen unites with three atoms of hydrogen, the result in each case is a molecule, and, according to the law of Avogadro, a gaseous molecule whether it consists of one atom or a hundred atoms occupies the same space.

**Ammonium Amalgam.**—A very curious substance which appears to consist of mercury and ammonium is formed when a solution of ammonium chloride is treated with a compound of sodium and mercury

known as sodium amalgam. The action is thought to take place thus:

$$2NH_4Cl + Na_2Hg = 2NaCl + (NH_4)_2Hg.$$

The product, ammonium amalgam, is unstable, breaking down very soon into ammonia, hydrogen, and mercury. It will be referred to again and somewhat more fully under the head of Mercury.

**Metallic Derivatives of Ammonium Compounds and of Ammonia.**—Ammonia acts upon a number of metallic salts, forming with them complex derivatives which in some cases appear to be ammonia, and in others ammonium, in which one or more hydrogen atoms are replaced by metal. Thus mercuric chloride, $HgCl_2$, acts upon ammonia, forming a compound of the formula $HgClNH_2$. This appears to be ammonium chloride in which two hydrogen atoms are replaced by a mercury atom, or as mercuric chloride in which one chlorine atom is replaced by the group $NH_2$, known as the amide group. According to the latter view the structure of this compound is represented by the formula $Hg{<}^{Cl}_{NH_2}$. Similarly, copper chloride, $CuCl_2$, forms a compound the composition of which is represented by the formula $CuCl_2.2NH_3$. It seems probable that this is ammonium chloride in which two hydrogen atoms are replaced by an atom of copper, $Cu{<}^{NH_3Cl}_{NH_3Cl}$. There are many such compounds, particularly of the metals mercury, copper, cobalt, and platinum. The structural formulas above given are to be regarded merely as suggestions. Experimental evidence in favor of them is lacking.

**Structure of Ammonium Compounds.**—In ammonia nitrogen is unquestionably trivalent. But what takes place when ammonia acts upon water, upon hydrochloric acid, and upon acids in general? What structure is to be ascribed to the ammonium compounds? The view generally held is that in the ammonium compounds nitrogen is quinquivalent. According to this, ammonia is an unsaturated compound, and when brought in contact

with water, hydrochloric acid, etc., it saturates itself. The conception is represented thus:

$$N\begin{Bmatrix} H \\ H \\ H \end{Bmatrix} + HCl = N\begin{Bmatrix} H \\ H \\ H \\ H \\ Cl \end{Bmatrix};$$

$$N\begin{Bmatrix} H \\ H \\ H \end{Bmatrix} + H_2O = N\begin{Bmatrix} H \\ H \\ H \\ H \\ OH \end{Bmatrix};$$

$$N\begin{Bmatrix} H \\ H \\ H \end{Bmatrix} + HNO_3 = N\begin{Bmatrix} H \\ H \\ H \\ H \\ NO_3 \end{Bmatrix}.$$

In all the resulting compounds the nitrogen is believed to be quinquivalent. It must be confessed that, while this is a convenient hypothesis, further evidence for or against it is desirable. One objection which may be raised to it is this. It is assumed that when the stable compound hydrochloric acid acts upon ammonia the hydrogen separates from the chlorine and both combine with nitrogen; but for nitrogen alone chlorine has very little attraction. This objection may not be a real one. It may be shown that, while chlorine has for nitrogen alone very little attraction, it has great attraction for nitrogen which is in combination with hydrogen.

**Hydrazine, $N_2H_4$.**—A compound closely related to ammonia and ammonium has recently been prepared by a complicated method which cannot be explained here. This is known as hydrazine. Its composition and molecular weight are represented by the formula $N_2H_4$. A large number of derivatives of hydrazine are known, and have been studied exhaustively. From what has been learned in regard to them it appears that the constitution of hydrazine is represented by the formula $\begin{matrix} NH_2 \\ | \\ NH_2 \end{matrix}$. Accord-

ing to this it bears to ammonia a relation similar to that which hydrogen peroxide is believed to bear to water:

$$
\begin{array}{ll}
OH_2 & NH_3 \\
OH & NH_2 \\
\overset{|}{OH} & \overset{|}{NH_3}.
\end{array}
$$

Hydrazine is a liquid that boils at $113°.5$ in a current of hydrogen. It acts upon acids much as ammonia does, forming the hydrazine salts.

**Hydroxylamine, $NH_2(OH)$.**—This compound is prepared by reducing nitric acid:

$$NO_2(OH) + 6H = NH_2(OH) + 2H_2O.$$

It can also be prepared by reduction of nitric oxide:

$$2NO + 6H = 2NH_2(OH).$$

Hydroxylamine is a solid consisting of leaflets or hard needles. It melts at $33°.05$, and boils at $58°$ under a pressure of 22 mm. When the water solution is evaporated, both ammonia and hydroxylamine pass over with the water. Its salts are easily obtained by treating the solution with acids:

$$
\begin{array}{ll}
NH_2(OH) + HCl & = NH_3(OH)Cl; \\
NH_2(OH) + HNO_3 & = NH_3(OH)NO_3.
\end{array}
$$

From the method of formation and the composition it appears that these salts are ammonium salts in which one hydrogen of the ammonium is replaced by hydroxyl. They should therefore be called *hydroxyl-ammonium salts.* One of the most characteristic properties of hydroxylamine is the ease with which it breaks down into ammonia, nitrogen, and water:

$$3NH_2OH = N_2 + NH_3 + 3H_2O.$$

If brought in contact with compounds capable of reduction, it reduces them, the nitrogen in these cases generally combining with oxygen to form nitrous oxide, $N_2O$. The reduction of cupric oxide, $CuO$, takes place according to the equation

$$2NH_2(OH) + 4CuO = N_2O + 2Cu_2O + 3H_2O.$$

By nascent hydrogen hydroxylamine is reduced to ammonia.

**Triazoic Acid, $N_3H$.**—This compound, which is also called *hydrazoic* and *hydronitric acid*, can be made by a number of reactions involving the use of complex organic substances. A simpler method consists in passing ammonia gas over heated metallic sodium, and then passing nitrous oxide, $N_2O$, over the resulting product, which is sodium amide. The following reaction takes place:

$$NH_2Na + N_2O = N_3Na + H_2O.$$

By dissolving in water the sodium salt thus formed, treating with dilute sulphuric acid, and distilling, a solution of the acid is obtained. The compound is a colorless liquid that boils at 37°. It has a fearfully penetrating odor, and produces bad effects upon one who inhales it. It is a strong acid resembling hydrochloric acid. It, as well as some of its salts, is extremely explosive. Its ammonium salt formed by direct union with ammonia is interesting as it has the composition $N_3NH_4$ or $N_4H_4$.

**Nitric Acid, $HNO_3$.**—This important chemical compound was first made, though not in pure condition, about the ninth century by distilling saltpeter, copper sulphate, and alum. The name nitric acid has its origin in the fact that the compound is formed from niter. In German it is called *Salpetersäure*, which literally translated is *saltpeter acid*. It has already been stated that the salts of this acid, particularly the potassium and sodium salts, occur very widely distributed in the earth, and that there is a great accumulation of the sodium salt in South America, whence the name Chili saltpeter. Wherever organic matter, particularly that of animal origin, undergoes spontaneous decomposition in the presence of basic substances, nitrates are formed, probably in consequence of the action of an organism known as the *nitrifying ferment*. This process of nitrification has already been referred to in a general way. It is one of great importance for the welfare of the human race, and indeed of most

living beings, as by its aid the useless nitrogenous sub-stances of dead plants and animals are converted back into the useful nitrates which in the soil aid the pro-cesses of plant growth.

Nitric acid can be formed by the action of electric sparks on nitrogen and oxygen in the presence of water. It is also easily formed by the action of oxidizing agents on ammonium compounds.

Nitric acid is always prepared by treating potassium or sodium nitrate with concentrated sulphuric acid. When sodium nitrate is treated with sulphuric acid action takes place thus:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

The salt formed in this way is primary sodium sulphate, or acid sodium sulphate. If sufficient of the saltpeter is present and the temperature is raised, a second reaction takes place, resulting in the formation of normal sodium sulphate:

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

But the temperature required for this reaction is so high that a considerable part of the nitric acid is decomposed. In the preparation of nitric acid, therefore, the first re-action is the one used, and for this purpose the sub-stances are brought together in a retort in the proportion of their molecular weights (about equal weights), and the retort gently heated. The nitric acid distils over slowly, and is condensed by cooling the receiver.

On the large scale the acid is made by bringing Chili saltpeter and concentrated sulphuric acid together in cast-iron cylinders or retorts.

Nitric acid is a colorless volatile liquid. It begins to boil at 86°, but at this temperature it undergoes partial decomposition into nitrogen peroxide, water, and oxygen:

$$2HNO_3 = 2NO_2 + H_2O + O.$$

It undergoes the same change slowly when exposed to the direct rays of the sun. In consequence of this de-

composition the distillate collected in the manufacture of nitric acid, and, in general, whenever the acid is distilled, always contains a considerable percentage of water, and is colored more or less yellow by the nitrogen peroxide present. In order to abstract the water from ordinary nitric acid it is mixed with concentrated sulphuric acid and slowly distilled; but even under these circumstances the product is colored in consequence of some decomposition, and it also contains some water. By conducting carbon dioxide gas through the gently warmed acid the nitrogen peroxide can be removed, and in this way an acid containing about 99.5 per cent of the compound $HNO_3$ has been obtained.

Pure nitric acid is a very active substance chemically. It gives up its oxygen readily and is itself thus reduced to other compounds of nitrogen and oxygen, or of nitrogen, oxygen, and hydrogen, as has already been pointed out. When it acts upon the metals it forms nitrates, metal atoms being substituted for the hydrogen. According to the conditions, nitrogen peroxide, $NO_2$, nitrous acid, $HNO_2$, nitric oxide, $NO$, nitrous oxide, $N_2O$, nitrogen, hydroxylamine, $NH_2(OH)$, and, finally, ammonia are formed by reduction of the acid. The formation of ammonia and of hydroxylamine by reduction of nitric acid has already been specially referred to. Of these reactions, that which gives nitric oxide, $NO$, is the one which commonly takes place on treating metals with nitric acid. The oxides $NO_2$ and $N_2O_3$ are themselves readily reduced to nitric oxide.

If the element upon which the acid acts has not the power to replace the hydrogen, the action consists in oxidation. This is shown in the action of strong nitric acid upon tin, phosphorus, carbon, sulphur, etc. In each case the highest oxidation-product is formed. Tin is converted into normal stannic acid, $Sn(OH)_4$; phosphorus into phosphoric acid, $PO(OH)_3$; carbon into carbon dioxide, $CO_2$; and sulphur into sulphuric acid, $SO_2(OH)_2$. It disintegrates carbon compounds very readily, converting them into their final products of oxidation. In contact with the skin it causes bad and dangerous wounds.

Upon some stable compounds of carbon it acts forming so-called *nitro-compounds*, very much as chlorine acts upon them forming chlorine substitution-products, as was explained under Chlorine. The formation of a nitro-compound takes place as represented in the equation

$$C_6H_6 + HO.NO_2 = C_6H_5.NO_2 + H_2O.$$

The compound $C_6H_6$ is benzene, and the compound $C_6H_5.NO_2$ is nitro-benzene.

The acid mostly used in the laboratory has the specific gravity 1.2 and contains 32 per cent nitric acid, $HNO_3$. The commercial acid contains about 68 per cent of the acid.

When a mixture of nitric acid and water is boiled under the ordinary atmospheric pressure it loses either water or nitric acid until it contains 68 per cent of the acid which passes over. This does not correspond to any definite hydrate of nitric acid, though it approximates the composition required by normal nitric acid, $N(OH)_5$, or $HNO_3 + 2H_2O$, and it is probable that this hydrate is the chief constituent of the mixture.

Nitric acid is a strong monobasic acid, forming salts of the general formula $MNO_3$, all of which are soluble in water. Because nitric acid is a strong acid, and all normal nitrates are soluble in water, nitric acid is one of the best solvents. On the other hand, the acid forms basic salts, some of which are difficultly soluble or insoluble in water. An example of such insoluble basic nitrates is the nitrate of bismuth of the formula $Bi\begin{cases} NO_3 \\ OH, \\ OH \end{cases}$ which is to be regarded as bismuth hydroxide one-third neutralized by nitric acid. There are some apparently complex salts of nitric acid which are derived from the normal acid, $N(OH)_5$, as, for example, the salt $HPb_3O_6N$, which should probably be expressed thus, $N\begin{cases} {}^O_O{>}Pb \\ {}^O_O{>}Pb \\ O.Pb.OH \end{cases}$, being a basic lead salt of the normal acid. There are.

further, some salts which are derived from the acid $NO(OH)_3$, which is formed by abstracting one molecule of water from normal nitric acid:

$$N(OH)_5 = NO(OH)_3 + H_2O.$$

By far the largest number of nitrates, however, are derived from the acid of the formula $HNO_3$.

**Red Fuming Nitric Acid** is formed in the manufacture of nitric acid from saltpeter and sulphuric acid if the temperature is raised to a sufficient extent to cause the acid sulphate to act upon the nitrate:

$$NaNO_3 + HNaSO_4 = Na_2SO_4 + HNO_3.$$

At this temperature the nitric acid undergoes considerable decomposition. The nitrogen peroxide formed is absorbed by the nitric acid, and the product thus obtained is the red fuming acid. It acts more energetically than nitric acid, and finds some applications in the laboratory and in the arts. When heated it gives off nitrogen peroxide, and if diluted with water it is changed to ordinary nitric acid, as nitrogen peroxide is decomposed by water, forming nitric acid and nitric oxide or nitrous acid, according to the temperature of the water.

*Nitro-hydrochloric Acid or Aqua Regia* is a liquid formed by mixing concentrated nitric and hydrochloric acids. It was called *aqua regia* because it can dissolve gold, the king of the metals. The active power of this liquid as a solvent of metallic substances is due to the fact that it gives off chlorine, and a compound of nitrogen, oxygen, and chlorine which readily gives up its chlorine. This compound has the composition represented by the formula $NOCl$, and it is best designated by the name *nitrosyl chloride*. The product of the action of nitro-hydrochloric acid upon a metal is the corresponding chloride.

**Nitrous Acid, $HNO_2$.**—When certain salts of nitric acid are reduced they yield the corresponding nitrites. Thus, when potassium nitrate is heated with metallic lead this reaction takes place:

$$KNO_3 + Pb = KNO_2 + PbO.$$

Indeed, if potassium nitrate is heated alone it loses oxygen and is converted into the nitrite :

$$2KNO_3 = 2KNO_2 + O_2 ;$$

but the reaction is not complete, and the salt thus obtained always contains more or less nitrate.

If an attempt is made to isolate nitrous acid from a nitrite the product is the anhydride, nitrogen trioxide, $N_2O_3$. Thus, if sulphuric acid is added to potassium nitrite the following reaction takes place :

$$2KNO_2 + H_2SO_4 = N_2O_3 + H_2O + K_2SO_4.$$

It may be that the first action is the liberation of nitrous acid, and that this then breaks down by loss of water. The two reactions are represented thus :

$$2KNO_2 + H_2SO_4 = 2HNO_2 + K_2SO_4 ;$$
$$2HNO_2 = N_2O_3 + H_2O.$$

A certain analogy will be observed between this action and that which takes place in the action of potassium hydroxide upon an ammonium salt, when ammonium hydroxide is probably first given off, and then breaks down into ammonia and water.

Salts are known which are derived from *normal nitrous acid*, $N(OH)_3$, but most of the nitrites are derived from the acid of the formula $NO(OH)$, which is to be regarded as formed from the normal acid by loss of one molecule of water :

$$N(OH)_3 = NO(OH) + H_2O.$$

**Hyponitrous Acid, $H_2N_2O_2$.**—The sodium salt of this acid is made by reducing sodium nitrite in solution by means of sodium amalgam :

$$2NaNO_2 + 8H = Na_2N_2O_2 + 4H_2O.$$

The acid can also be made by oxidation of hydroxylamine.

It is a solid consisting of white crystalline plates. It is very explosive when freed from water. In water solu-

tion it is much more stable, but at the ordinary tempera-
ture it breaks down gradually, the principal products
being nitrous oxide and water :

$$H_2N_2O_2 = N_2O + H_2O.$$

It would appear from this that nitrous oxide, $N_2O$, bears
to hyponitrous acid the relation of an anhydride, but
salts of the acid cannot be obtained from nitrous oxide
directly. The molecular weight of hyponitrous acid in
solution has been determined, and the result shows
that the acid has the double formula $H_2N_2O_2$. Its
structure is probably to be represented by the for-
mula $\begin{matrix} N(OH) \\ \| \\ N(OH) \end{matrix}$.

**Nitrous Oxide, $N_2O$.**—This compound can be obtained
by reduction of nitric acid, and is sometimes formed in
considerable quantity when copper is treated with the
concentrated acid, though when made in this way it
is always mixed with a large proportion of nitric oxide.
The best way to make it is to heat ammonium nitrate,
$NH_4NO_3$, which breaks down into nitrous oxide and water :

$$NH_4NO_3 = N_2O + 2H_2O.$$

In the same way we have seen that ammonium nitrite
breaks down into free nitrogen and water when heated :

$$NH_4NO_2 = N_2 + 2H_2O.$$

In these reactions we see exhibited the tendency of
hydrogen and oxygen to combine at elevated tempera-
tures. At ordinary temperature this tendency is not
strong enough to cause a disturbance of the equilibrium
of the parts of the compound. As the temperature is
raised and the equilibrium thus disturbed, the affinity
of the hydrogen for the oxygen asserts itself. The two
elements combine to form water, and the decomposition
above represented takes place.

Nitrous oxide is a colorless, transparent gas which has

a sweetish taste and odor. Its specific gravity is 1.527. It is somewhat soluble in water; one volume of water at 0° dissolving somewhat more than its own volume of the gas. It supports combustion almost as well as pure oxygen. Some substances which burn in oxygen do not, however, burn in nitrous oxide. Sulphur which burns in oxygen is extinguished in nitrous oxide, unless it is previously heated to a high temperature. To understand the action of this compound in supporting combustion it must be borne in mind that, when anything burns in oxygen, the oxygen molecules must first be broken down into atoms before the combination can take place. Thus, when carbon and oxygen are brought together we have at first a condition represented by these symbols :

$$O_2 + C,$$

the question as to the condition of the carbon being left open. When the temperature is raised to a sufficiently high point the condition is represented thus :

$$O + O + C ;$$

and now the reaction takes place :

$$O + O + C = CO_2.$$

In the act of burning in free oxygen, therefore, there is always a certain resistance to be overcome. Now, when a combustible substance is brought into a gas which gives up its oxygen easily the condition is much like that in free oxygen. If the temperature is raised the gas is decomposed, and the oxidation then follows. In the case of nitrous oxide this decomposition takes place :

$$N_2O = N + N + O,$$

and this oxygen in the atomic condition effects the oxidation.

When inhaled, nitrous oxide causes a kind of intoxication, which is apt to show itself in the form of hysterical laughing. Hence the gas is called *laughing gas*. In-

haled in larger quantity it causes unconsciousness and insensibility to pain. It is therefore used extensively to prevent pain in some surgical operations, particularly in extracting teeth.

When subjected to a low temperature and high pressure the gas is easily liquefied, and enclosed in properly constructed metallic cylinders the liquid is now sent into the market. In order to get the gas it is only necessary to open the stop-cock of the cylinder. When the liquid comes in contact with the air it rapidly turns to gas, and the temperature is very much lowered in consequence. This causes a part of the liquid to solidify.

**Nitric Oxide, NO.**—This is the most stable compound of nitrogen and oxygen, and is the common product of the reduction of nitric acid. Thus, when nitric acid acts upon copper and other metallic elements the chief product is generally nitric oxide, though, as we have seen, the reduction may be carried farther. The principal action in the case of copper is represented thus:

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Considering the ease with which nitric acid gives up its oxygen, and the ease with which copper takes up oxygen, it is probable that the copper abstracts oxygen directly from the acid as represented thus:

$$2HNO_3 + 3Cu = CuO + H_2O + 2NO.$$

In this case the copper oxide would at once form copper nitrate with the excess of nitric acid:

$$6HNO_3 + 3CuO = 3Cu(NO_3)_2 + 3H_2O.$$

Or, combining the two equations, the total action is represented in the same way as it is above. The nitric acid must not have a specific gravity higher than 1.2, and the temperature must be kept down, otherwise the reduction of the nitric acid is carried farther and considerable nitrous oxide is formed.

It is possible that to some extent the hydrogen liber-ated from the acid may act as a reducing agent, thus causing the formation of the lower oxides of nitrogen, as, for example,

$$2HNO_3 + 6H = 2NO + 4H_2O.$$

A good method for making pure nitric oxide consists in treating ferrous chloride, $FeCl_2$, with saltpeter. The re-action is represented thus:

$$3FeCl_2 + KNO_3 + 4HCl = 3FeCl_3 + KCl + 2H_2O + NO.$$

The reducing action is here effected by the ferrous chloride, $FeCl_2$, which tends to pass over into ferric chloride, $FeCl_3$, in the presence of hydrochloric acid, and anything which has the power to take up hydrogen. With hydrochloric acid alone it does not form ferric chloride, but if any reducible compound is present ac-tion takes place thus:

$$2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O.$$

In the above reaction saltpeter furnishes the oxygen, and it is consequently reduced and breaks down, yielding nitric oxide, while the potassium forms potassium chlo-ride with chlorine.

Nitric oxide is a colorless, transparent gas. Its most remarkable property is its power to combine directly with oxygen when the two are brought together. The act of combination is not accompanied by the appear-ance of light, though heat is evolved. In the reaction which takes place at ordinary temperatures nitrogen peroxide, $NO_2$, is formed:

$$NO + O = NO_2.$$

The product is a colored gas, and the change of the color-less nitric oxide to this colored product can therefore easily be recognized. This reaction is, further, the chief cause of the reddish-brown fumes seen when nitric acid acts upon metals and other elements. At a low temper-ature some nitrogen trioxide is formed when oxygen acts upon nitric oxide.

From what has already been said, it will appear that in nitric oxide the oxygen and nitrogen are more firmly united than in the other oxides. Most burning substances are extinguished when introduced into it, though a few when heated in it to a high temperature extract all or a part of the oxygen. Zinc and iron extract half the oxygen and convert nitric oxide into nitrous oxide. Potassium and sodium decompose it, leaving the nitrogen free.

A curious reaction by means of which it is possible to separate nitric oxide from other gases takes place, when the oxide is passed into a solution of ferrous sulphate, $FeSO_4$. Under these circumstances an unstable dark-colored compound is formed, which appears to have the composition $FeSO_4 + 2NO$. When the solution containing it is heated the pure gas is given off.

By nascent hydrogen nitric oxide is reduced to ammonia and hydroxylamine.

**Nitrogen Trioxide, $N_2O_3$.**—This oxide is formed by addition of oxygen to nitric oxide at low temperatures; by decomposition of the nitrites by means of acids; and by the combination of nitric oxide with the peroxide at a temperature below $-21°$. The gas given off when nitric acid is reduced with starch or arsenious oxide, $As_2O_3$, appears to be a mixture of nitric oxide and the peroxide. Pure nitrogen trioxide is a liquid of an indigo-blue color. At a temperature below $0°$ it undergoes partial decomposition into nitrogen peroxide and nitric oxide:

$$N_2O_3 = NO + NO_2.$$

With cold water nitrogen trioxide undergoes decomposition accompanied by an evolution of nitric oxide. Possibly this reaction takes place:

$$3N_2O_3 + H_2O = 2HNO_3 + 4NO.$$

By treating the oxide with a solution of sodium hydroxide or potassium hydroxide the corresponding nitrite is formed:

$$2KOH + N_2O_3 = 2KNO_2 + H_2O.$$

**Nitrogen Peroxide, $NO_2$.**—When nitric oxide and oxygen are brought together in the proportion of 2 volumes of the former to 1 volume of the latter they combine completely to form nitrogen peroxide. These relations will be readily understood when it is borne in mind that 2 molecules of nitric oxide require 1 molecule of oxygen to effect the change, as is shown in the equation

$$2NO + O_2 = 2NO_2.$$

The compound is most easily obtained by heating lead nitrate, when nitrogen peroxide and oxygen are given off, and lead oxide remains behind in the vessel:

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

If the gases are passed through a tube surrounded by a freezing mixture the peroxide is condensed to the form of liquid, while the oxygen passes on. When perfectly dry the peroxide is easily solidified. It acts energetically upon compounds which have the power to take up oxygen. When treated with water it undergoes decomposition. If the temperature is low, nitrous and nitric acids are formed:

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$

If the water is hot, however, the products are nitric acid and nitric oxide:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The nitric oxide thus formed will take up oxygen from the air and yield nitrogen peroxide again, and this, in contact with hot water, will be decomposed, forming nitric acid and nitric oxide, until all the peroxide is converted into nitric acid.

The determinations of the specific gravity of the gas from the peroxide show that at low temperatures the molecular formula is $N_2O_4$, but that when the temperature 150° is reached the molecule is represented by the formula $NO_2$. The compound appears therefore to undergo gradual decomposition or dissociation by heat, so that until the temperature 150° is reached the gas is a mixture of the compounds $N_2O_4$ and $NO_2$.

**Nitrogen Pentoxide, $N_2O_5$.**—This compound, which bears to nitric acid the relation of an anhydride, is formed by passing chlorine over silver nitrate and condensing the product. The reaction takes place thus:

$$2AgNO_3 + Cl_2 = N_2O_5 + 2AgCl + O.$$

It is also formed by treating nitric acid with phosphorus pentoxide, $P_2O_5$, a compound which has a very marked power to unite with water. The action is represented thus:

$$2HNO_3 = N_2O_5 + H_2O.$$

The pentoxide is a crystallized substance, which readily decomposes into nitrogen peroxide and oxygen. In consequence of the ease with which it gives up its oxygen it acts violently upon many oxidizable substances. With water it forms nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

**Structure of the Compounds of Nitrogen with Oxygen and Hydrogen.**—Our knowledge of the structure of the compounds with which we have just been dealing is unsatisfactory. There is at present no way of deciding whether in a compound like nitrous oxide, for example, the oxygen is in combination with both nitrogen atoms: there are no reactions of the compound which throw any light upon this question. Similar difficulties are met with in connection with the other compounds of nitrogen and oxygen. As was remarked on page 264, the simplest view which can be held in regard to these oxides is that in them the nitrogen is univalent, bivalent, trivalent, quadrivalent, and quinquivalent, a view which is expressed by the following formulas:

$$\frac{N}{N}{>}O, \quad N{=}O, \quad \begin{array}{c} N{=}O \\ {>}O \\ N{=}O \end{array}, \quad O{=}N{=}O, \quad \begin{array}{c} O{=}N{=}O \\ {>}O \\ O{=}N{=}O \end{array}.$$

These formulas are, however, purely speculative and represent nothing known to us. But if the valence of

nitrogen can vary in this way, we may also conceive that
the oxygen is univalent in all the compounds except
nitrous oxide. Thus nitric oxide may be represented by
the formula N–O, nitrogen peroxide by $N<_O^O$, etc. On
the other hand, there is an unmistakable tendency on
the part of the elements to act either with even valences,
as 2, 4, 6, etc., or with odd, as 1, 3, 5, etc. This is beauti-
fully shown by the members of the chlorine group and
those of the sulphur group. It has been pointed out
that the relations between the compounds of chlorine,
bromine, and iodine can be explained, by assuming that
these elements are univalent, trivalent, quinquivalent,
and septivalent; and that the relations between the
compounds of sulphur, selenium, and tellurium can be
equally easily explained by assuming that these elements
are bivalent, quadrivalent, and sexivalent. In the case
of nitrogen and the elements belonging to the same group
we should naturally expect to find a similar law of com-
position holding good. As far as the hydroxyl deriva-
tives, represented by nitrous acid and nitric acid, are
concerned, the same regularity is observed as in the case
of sulphur. In nitric acid the nitrogen is probably quin-
quivalent, and in nitrous acid trivalent. Further, in
ammonia nitrogen is trivalent, while it is probably quin-
quivalent in the ammonium compounds, as has been
pointed out (see p. 275). It is clear that nitrogen tends
to act either as a trivalent or quinquivalent element.
Whether it ever acts as a univalent element it is impos-
sible to say, for, while the existence of the compound
$N_2O$ seems to show that it does, this same compound
may be explained on the assumption that in it the ni-
trogen is trivalent, as shown in the formula $_{\parallel}^{N}>O$; and
indeed there is no difficulty in assuming any desired
valence for the nitrogen. Taking the compound nitric
oxide, there seems to be no escape here from the con-
clusion that the nitrogen is bivalent if the oxygen is bi-
valent; and the compound forms a striking exception to

the rule above referred to that the valence of an element generally changes from odd to odd or from even to even. It may be said that this compound is unsaturated, and that one of its bonds is unemployed, a condition which may be symbolized by this expression, $-N=O$, but this does not help us out of the difficulty, and, further, this conception is not in accordance with the fact that nitric oxide takes up one atom of oxygen to form nitrogen peroxide, $NO_2$. And then the question arises, What is the structure of this last-mentioned compound? Should it be represented thus: $O=N=O$? If so the nitrogen is quadrivalent. But it passes readily into the form $N_2O_4$. It may be that this act consists simply in the union of the two molecules by means of the fifth bond of quinquivalent nitrogen, the structure of the resulting molecule being represented thus: $\begin{matrix} O=N=O \\ | \\ O=N=O \end{matrix}$. All this is, however, almost pure speculation, and, at the present stage of our knowledge of the subject of structure, the above formulas have very little value. Still it must not be forgotten that the structure of all chemical compounds is a legitimate subject of investigation.

When we come to the acids of nitrogen it is seen, as has already been pointed out, that these can be explained very satisfactorily by the aid of the same hypothesis that served so well in dealing with the acids of iodine and of sulphur. Nitric acid is to be regarded as derived from the maximum hydroxyl compound of quinquivalent nitrogen, known as *normal nitric acid*, by loss of water; and in a similar way nitrous acid is to be regarded as derived from the maximum hydroxyl compound of trivalent nitrogen, or *normal nitrous acid*, by loss of water. A few salts are known which appear to be derived from the normal acids, but for the most part all the hydrogen atoms of these normal acids are not replaceable by metals, and the formation of salts generally involves a breaking down of the compound into water and the common form of the acid.

**Compounds of Nitrogen with the Elements of the Chlorine Group.**—Notwithstanding the ease with which chlo-

rine combines with most elements, and the stability of the compounds which it forms with them, its compound with nitrogen is extremely unstable. It can be made by the action of chlorine on ammonia, and by decomposing a solution of ammonium chloride by means of an electric current. In the latter case chlorine is liberated at one of the poles and then acts upon the ammonium chloride :

$$NH_4Cl + 6Cl = 4HCl + NCl_3.$$

It appears that when chlorine acts upon ammonia different products are formed by successive replacement of the hydrogen atoms of the ammonia by chlorine, thus :

$$NH_3 \quad + Cl_2 = NH_2Cl + HCl ;$$
$$NH_2Cl + Cl_2 = NHCl_2 + HCl ;$$
$$NHCl_2 + Cl_2 = NCl_3 \quad + HCl.$$

According to this, the trichloride of nitrogen is the final product of the substituting action of chlorine upon ammonia. The compound is an oil, which undergoes decomposition very readily. It is, indeed, one of the most explosive substances known. It is decomposed by heat, and especially by contact with certain substances, among which are oil of turpentine and caoutchouc. It is slowly decomposed by water, though, probably owing to the slight affinity of nitrogen for oxygen, the decomposition does not take place as readily as that of the compounds of sulphur and chlorine. Direct sunlight causes explosion of the chloride.

When ammonia is treated with iodine reactions take place similar to those which take place with chlorine. The products are the iodides of nitrogen, the final product of the action being the tri-iodide, $NI_3$. These compounds, like the corresponding chlorine compounds, are extremely explosive. The simplest way to prepare them is to place a little powdered iodine on a filter and pour concentrated ammonia over it. The substance should be made in only very small quantities at a time. When dried it decomposes with violent explosion by contact even with soft substances; and it will also ex-

plode if left entirely undisturbed. The different compounds called nitrogen iodide are slowly decomposed by water.

**Compounds of Nitrogen with the Members of the Sulphur Group.**—Nitrogen combines with sulphur forming two compounds, $N_4S_4$ and $N_5S_2$, both of which are well characterized. Among the most interesting compounds containing sulphur and nitrogen is that which has been referred to as nitrosyl-sulphuric acid in connection with the account of the manufacture of sulphuric acid. It is formed by the action of sulphur dioxide on fuming nitric acid :

$$NO_2(OH) + SO_2 = SO_3 {<}^{NO_2}_{OH};$$

also in the manufacture of sulphuric acid by the action of sulphur dioxide, water, and oxygen upon a mixture of nitrogen peroxide and nitric oxide :

$$2SO_2 + H_2O + N_2O_3 + 2O = 2SO_2 {<}^{NO_2}_{OH};$$

and by the action of the nitrogen peroxide upon sulphuric acid :

$$2NO_2 + SO_2 {<}^{OH}_{OH} = SO_2 {<}^{NO_2}_{OH} + HNO_3.$$

When treated with water it breaks down into sulphuric acid and nitrogen trioxide. It will be remembered that, in order to prevent loss of oxides of nitrogen in the sulphuric acid factories, the gases are brought in contact with concentrated sulphuric acid in the Gay Lussac tower before being allowed to escape. The oxides form with sulphuric acid compounds similar to nitrosyl-sulphuric acid, and when these are diluted with "chamber acid" and heated by the hot gases from the sulphur furnace the oxides of nitrogen are given up.

# CHAPTER XVII.

ELEMENTS OF FAMILY V, GROUP B:
PHOSPHORUS—ARSENIC—ANTIMONY—BISMUTH.
THE ELEMENTS AND THEIR COMPOUNDS WITH
HYDROGEN.

**General.**—The elements of this group bear to nitrogen very much the same relations that the members of the sulphur group bear to oxygen, and those of the chlorine group bear to fluorine. In general they form compounds of the same character and of similar composition. At the same time gradations in properties are noticed in passing from one end of the group to the other. Like nitrogen, the elements of the group are strongly marked acid-formers, though this character grows less marked from nitrogen to bismuth. Antimony is both an acid-forming and a base-forming element, while bismuth is more basic than acid. The stability of the hydrogen compounds decreases from nitrogen to antimony; while bismuth does not form a compound with hydrogen. Ammonia, as we have seen, is strongly basic; the corresponding compound of phosphorus and hydrogen has weak basic properties, while those of arsenic and antimony have no basic properties. These hydrogen compounds correspond in composition to ammonia. They are:

$$NH_3: \quad PH_3 \quad AsH_3 \quad SbH_3$$

With chlorine they all form compounds corresponding to nitrogen trichloride, and phosphorus and antimony form compounds in which they are quinquivalent, while

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bismuth forms a chloride, $Bi_2Cl_4$, in addition to the tri-chloride.   The compounds referred to are:

|          |          |          |          | $Bi_2Cl_4$ |
|----------|----------|----------|----------|----------|
| $NCl_3$: | $PCl_3$  | $AsCl_3$ | $SbCl_3$ | $BiCl_3$ |
|          | $PCl_5$  |          | $SbCl_5$ |          |

They all form two oxides corresponding to nitrogen tri-oxide and pentoxide:

| $N_2O_3$: | $P_2O_3$ | $As_2O_3$ | $Sb_2O_3$ | $Bi_2O_3$ |
|-----------|----------|-----------|-----------|-----------|
| $N_2O_5$: | $P_2O_5$ | $As_2O_5$ | $Sb_2O_5$ | $Bi_2O_5$ |

No one of the elements of the group forms as great a variety of compounds with oxygen as nitrogen does. Antimony, however, forms the oxide $Sb_2O_4$, correspond-ing to nitrogen peroxide, $N_2O_4$; and bismuth forms the oxide $Bi_2O_2$ or $BiO$, corresponding to nitric oxide, $NO$.

The hydroxyl compounds or acids, like those of nitro-gen, are related to the maximum hydroxyl compounds of the elements with the valence 5, and to the maximum hydroxyl compounds of the elements with the valence 3. That is to say, they may be regarded as derived from a hydroxide of the general formula $M(OH)_5$, and another of the formula $M(OH)_3$.  Where M is nitrogen these acids break down to the forms $NO_2(OH)$ and $NO(OH)$ by loss of one or two molecules of water.   In the case of the elements of the phosphorus group, however, the breaking down is not generally carried as far as with nitrogen. The general rule is the same as in the sulphur and chlo-rine groups : the normal acid breaks down to form com-pounds containing the same number of hydrogen atoms as the hydrogen compounds of the elements.   Thus the hydroxyl derivatives of chlorine generally break down to form compounds containing one atom of hydrogen, or the same number that is contained in the hydrogen compound, hydrochloric acid, thus: $Cl(OH)_7$ yields $ClO_3(OH)$; $Cl(OH)_5$ yields $ClO_2(OH)$, etc.   So, also, in the sulphur group, $S(OH)_6$ yields $SO_2(OH)_2$, etc., the number of hy-drogen atoms in the common form of the acid being the same as that in the hydrogen compound of sulphur, $SH_2$.

This rule does not hold good for nitrogen, for the tendency here is to break down to compounds containing one atom of hydrogen. On the other hand, phosphorus, arsenic, and antimony follow the rule, the principal acids of these elements containing three atoms of hydrogen in the molecule. As already stated, there are two series of these represented by the following formulas:

$$H_3PO_3 \qquad H_3AsO_3 \qquad H_3SbO_3$$
$$H_3PO_4 \qquad H_3AsO_4 \qquad H_3SbO_4$$

Besides the above, however, phosphorus forms several other acids. The principal ones bear simple relations to the acid $H_3PO_4$, which is called orthophosphoric acid. The simplest view in regard to the acid of phosphorus of the formula $H_3PO_4$, and the corresponding compounds of arsenic and antimony, is that it is derived from the corresponding normal acid by loss of one molecule of water. Thus, normal phosphoric acid is $P(OH)_5$. By loss of one molecule of water this yields ordinary or orthophosphoric acid:

$$P(OH)_5 = PO(OH)_3 + H_2O.$$

Normal phosphorous acid is $P(OH)_3$. Whether ordinary phosphorous acid has this structure is a question very difficult to answer at present. By loss of another molecule of water orthophosphoric acid is converted into *metaphosphoric acid*, which in composition corresponds to nitric acid. Its formation is represented thus:

$$PO(OH)_3 = PO_2(OH) + H_2O.$$

The series of phosphorus acids, $H_3PO_2$, $H_3PO_3$, and $H_3PO_4$ is strongly suggestive of the series of sulphur acids, $H_2SO_2$, $H_2SO_3$, and $H_2SO_4$, and of the series of chlorine acids, $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$.

Arsenic and antimony also form acids corresponding to metaphosphoric acid, known respectively as *metarsenic* and *metantimonic acids.*

By elimination of one molecule of water from two molecules of ordinary phosphoric acid there is formed an acid $H_4P_2O_7$, known as *pyrophosphoric acid*, which bears to ordinary phosphoric acid much the same relation that pyrosulphuric or disulphuric acid bears to ordinary sulphuric acid :

$$SO_2 {<}^{OH}_{OH} \atop SO_2 {<}^{OH}_{OH} = {SO_2 {<}^{OH} \atop SO_2 {<}_{OH}}{>}O + H_2O.$$

$$PO {<}^{OH}_{OH} {\atop{^{OH}}} \atop PO{<}^{OH}_{OH}{\atop{_{OH}}} = {PO {<}^{OH}_{OH} \atop PO{<}_{OH}^{OH}}{>}O + H_2O.$$

Ordinary arsenic and antimonic acids yield corresponding derivatives known as *pyroarsenic* and *pyroantimonic acids*. The elements of the phosphorus group form compounds with oxygen and chlorine known as the oxychlorides, which in general resemble the oxychlorides of the members of the sulphur group. Examples of these compounds are phosphorus oxychloride, $POCl_3$, antimony oxychloride, $SbOCl$, and bismuth oxychloride, $BiOCl$. Phosphorus oxychloride is readily decomposed by water, forming phosphoric and hydrochloric acids :

$$PO {\begin{cases} Cl \\ Cl \\ Cl \end{cases}} + {\begin{matrix} HOH \\ HOH \\ HOH \end{matrix}} = PO {\begin{cases} OH \\ OH \\ OH \end{cases}} + 3HCl.$$

The oxychlorides of antimony and bismuth are not completely decomposed by water. This is in accordance with the fact to which attention has been called that the chlorides of the acid-forming elements are in general easily decomposed by water and converted into hydroxyl compounds, while the chlorides of the base-forming elements are not readily decomposed in this way, but, on the contrary, their oxides and hydroxides are, as a rule,

readily converted into chlorides by hydrochloric acid. Elements which, like antimony and bismuth, play the part of base-formers and acid-formers form stable oxychlorides.

Of the elements of this group phosphorus occurs most abundantly in nature, arsenic and antimony next, and bismuth least abundantly. Arsenic and bismuth occur to some extent in the uncombined condition. Phosphorus and antimony occur in combination. All the elements of the group find applications in the arts, either as the elements or in the form of compounds.

## Phosphorus, P (At. Wt. 30.79).

**Occurrence.**—The name phosphorus is derived from the Greek $\phi\hat{\omega}\varsigma$, light, and $\phi\acute{\epsilon}\rho\epsilon\iota\nu$, to carry, on account of the fact that it always gives light and takes fire very easily. The element occurs in nature in the form of phosphates derived from orthophosphoric acid, $H_3PO_4$. The chief of these is calcium phosphate, $Ca_3(PO_4)_2$, which is the principal constituent of the minerals *phosphorite* and *apatite,* and of the ashes of bones. The phosphates, like the nitrates, are widely distributed in the soil and are of fundamental importance in the process of plant life. The phosphates found in the bones are taken into the animal body in the food. All plants used as food contain small quantities of the phosphates which they get from the soil. The phosphates taken into the body are partly given off in the excrement and urine, and it was in an examination of urine made in the hope of finding the philosopher's stone that phosphorus was first discovered in 1669. At present phosphorus is made almost entirely from bones.

**Preparation.**—Besides the phosphates, considerable quantities of organic materials are contained in bones. When the bones are burned the organic materials pass off for the most part in the form of carbon dioxide, water, and volatile compounds containing nitrogen, and the so-called mineral or earthy portions, the chief constituent of which is tertiary calcium phosphate, or phosphoric

acid in which all the hydrogen is replaced by calcium, remain behind. As calcium is bivalent and there are three atoms of hydrogen in the molecule of phosphoric acid, $H_3PO_4$, the simplest way in which all the hydrogen atoms of the acid can be replaced by calcium is that represented by the formula $Ca_3(PO_4)_2$, the six atoms of hydrogen in two molecules of the acid being replaced by three bivalent atoms of calcium. The problem now is to isolate the phosphorus from this calcium phosphate. The salt is insoluble in water, and there is no simple way by which the phosphorus can be set free from it. When it is treated with sulphuric acid calcium sulphate which is difficultly soluble is deposited and phosphoric acid is set free and remains in solution. The reaction is represented as follows :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4.$$

The calcium sulphate, or gypsum, is allowed to settle and is then filtered off and washed. The solution of phosphoric acid is evaporated until it has the specific gravity 1.325 to 1.5. Then it is mixed with coarsely-ground wood charcoal, coke, or sawdust, and carefully dried in a cast-iron pot or muffle furnace. In this process the orthophosphoric acid, $H_3PO_4$, is converted into metaphosphoric acid, $HPO_3$,

$$H_3PO_4 = HPO_3 + H_2O ;$$

and in case sawdust is used this is changed, so that the resulting mixture consists of charcoal and metaphosphoric acid. This mixture is next subjected to distillation in clay retorts, when the metaphosphoric acid is reduced according to the following equation :

$$2HPO_3 + 6C = H_2 + 6CO + 2P.$$

The phosphorus passes over in the form of vapor, and is collected under water. The crude phosphorus thus obtained must be subjected to a cleansing process before it can be used. For this purpose it is pressed, while in the molten condition under water, through chamois leather, or it is distilled again from iron retorts ; or, still better, it is treated with chromic acid as follows : It is fused under water, then a little potassium or sodium

bichromate in solution is added, and afterwards an equivalent proportion of sulphuric acid, and the whole allowed to stand for two hours or more. The phosphorus is then washed with hot water, and after being siphoned off it is filtered through canvas bags. The phosphorus is then cast into sticks in tin tubes. In this form it generally comes into the market.

At the time of the last report available there were manufactured in one year about 1200 tons of phosphorus in two factories, one of which is in England and the other in France. Quite recently phosphorus has been manufactured to some extent in Sweden.

**Properties.**—Ordinary phosphorus is colorless or slightly yellowish, translucent, and at ordinary temperatures it can be cut like wax, but it becomes hard and brittle at low temperatures. It melts at 44°, and boils at 290°. It is insoluble in water. When kept under water for any length of time in dispersed light it becomes opaque, crystalline on the surface, and yellow. It is soluble in carbon disulphide, and crystallizes when deposited from this solution. It gives off fumes in contact with the air, and emits a pale light which is known as a phosphorescent light. It is very poisonous, the inhalation of the vapor in small quantities causing very serious disturbance of the system. The workmen in the factories where phosphorus is made or used are frequently affected by phosphorus-poisoning. Among the prominent symptoms is gradual decomposition of the bones. When taken into the stomach phosphorus also acts as a poison and causes death. When heated in the air it takes fire at 50°. It also takes fire by rubbing, and it must be handled with the greatest care, as wounds caused by it are dangerous and difficult to heal. When it burns in the air it is converted into the pentoxide, $P_2O_5$, which is also the product of its combustion in oxygen, as we have seen. It combines also with other elements directly, frequently with evolution of light. Thus, when it is brought together with chlorine, bromine, and iodine, it forms the compounds $PCl_3$, $PBr_3$, and $PI_3$. It also combines with sulphur. When a piece is put in water and the water boiled, a part of the phosphorus

passes over, and if the water vapor is condensed in a glass tube in a dark room, it is seen to be phosphorescent. This furnishes a convenient method for its detection, as, for example, in a case of suspected poisoning by phosphorus.

Owing to its strong tendency to combine with oxygen, it abstracts the element from some of its compounds. Thus, if a solution of phosphorus in carbon disulphide is added to a solution of copper sulphate, metallic copper is thrown down, while at the same time copper phosphate and a compound of copper and phosphorus are formed.

When phosphorus is left for a long time under water and subjected to the action of light, it becomes at first yellow, then reddish, and finally red. The same change takes place when phosphorus is heated for a time in an atmosphere which is free from oxygen; and rapidly when it is heated to 300° in an hermetically sealed tube. The red substance thus obtained has properties entirely different from those of ordinary phosphorus. It is a red powder, which frequently has a crystalline structure. It does not emit light. It does not melt at a low temperature. It is not poisonous, and cannot be easily ignited. Further, it is perfectly insoluble in carbon disulphide. In every respect this red modification of phosphorus conducts itself as a much less active substance chemically than ordinary phosphorus. In an atmosphere of carbon dioxide it is converted into ordinary phosphorus when heated to 261°, and if heated to this temperature in the air it takes fire, and then forms the same product that ordinary phosphorus does in burning.

When phosphorus is heated with lead for eight to ten hours to a very high temperature in sealed tubes from which the air has been exhausted, and the whole then allowed to cool, the surface of the lead is found covered with black, laminated crystals, which undergo no change in the air. Crystals are also found in the interior of the lead. This variety of phosphorus is called *crystallized, metallic phosphorus* on account of the metallic lustre. It is not as volatile as the ordinary variety.

When the vapor of phosphorus is suddenly cooled by ice water in an atmosphere of hydrogen, it is deposited in the form of a snow-white powder on the surface of the water. Under water this variety undergoes very little change even when exposed for a long time to the action of the sunlight. When exposed to the air on filter-paper it gives off dense fumes, and then melts, forming ordinary phosphorus, but it does not generally take fire under these circumstances.

Treated with oxidizing agents, as, for example, nitric acid, phosphorus is slowly converted into phosphoric acid, just as sulphur is converted into sulphuric acid under the same conditions.

**Applications of Phosphorus.**—Phosphorus is used principally in the manufacture of matches and as a poison for vermin. Various mixtures are used for making matches. Nearly all of them contain phosphorus together with some oxidizing compound, and some neutral substance to act as a medium for holding the constituents together. An example is a mixture consisting of 2 parts phosphorus, 1 part manganese dioxide, 3 parts chalk, ⅓ part lamp-black, and 5 parts glue. The mixture used in the manufacture of the so-called "safety matches" consists of potassium chlorate, potassium dichromate, minium, and antimony trisulphide. This will not ignite by simple friction, but will ignite when drawn across a paper upon which is a mixture of red phosphorus and antimony pentasulphide.

**Compounds of Phosphorus with Hydrogen.**—There are three compounds of phosphorus with hydrogen, a gaseous compound of the formula $PH_3$, corresponding to ammonia; a liquid of the formula $PH_2$, or $P_2H_4$, corresponding to hydrazine; and a solid of the formula $P_2H_3$, or $P_4H_2$.

**Phosphine, Gaseous Phosphuretted Hydrogen, $PH_3$.**—This compound is formed when phosphorous or hypophosphorous acid is heated. The decompositions take place as represented in these equations:

$$4H_3PO_3 = 3H_3PO_4 + PH_3;$$
$$2H_3PO_2 = H_3PO_4 + PH_3.$$

We see here an example of the same kind of action that was referred to in connection with the sulphur compounds. It will be remembered that, in general, when a salt of any oxygen acid of sulphur except sulphuric acid is heated it is converted into the sulphate, and that the other elements arrange themselves in simpler forms of combination. Thus, when sodium thiosulphate is heated it is converted into sodium sulphate and sodium pentasulphide, as represented in the following equation:

$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5.$$

So also sodium sulphite yields sodium sulphate and sodium sulphide:

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

Other ways of making phosphine are: (1) By treating a strong solution of potassium hydroxide with phosphorus, when reaction takes place as follows:

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

The compound $KH_2PO_2$ is known as potassium hypophosphite, being derived from hypophosphorous acid, $H_3PO_2$. (2) By treating zinc phosphide with dilute hydrochloric acid. Assuming that zinc phosphide has the composition represented by the formula $Zn_3P_2$, the reaction with hydrochloric acid takes place according to the equation

$$Zn_3P_2 + 6HCl = 3ZnCl_2 + 2PH_3.$$

(3) By treating phosphonium iodide, $PH_4I$, with water or a dilute solution of potassium hydroxide:

$$PH_4I + H_2O = PH_3 + HI + H_2O;$$
$$PH_4I + KOH = PH_3 + KI + H_2O.$$

When made from phosphorus and potassium hydroxide it always contains a considerable proportion of hydrogen, for the reason that potassium hypophosphite gives off hydrogen when heated with a solution of potassium hydroxide. From calcium phosphide and from phosphonium iodide it can be obtained in pure condition.

Phosphine is a colorless gas with an unpleasant, gar-lic-like odor. It is insoluble in water, and is poisonous. It burns, but does not take fire spontaneously when pure. When burned with free access of air the products of combustion are phosphorus pentoxide and water:

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O\ ;$$

whereas when it is burned in a cylinder so that the air has not free access to it, the products are water and phosphorus, which is deposited in a reddish layer upon the glass.

Although pure phosphine does not take fire spontane-ously when brought in contact with the air, the gas made by any one of the methods above referred to is pretty sure to contain some of the liquid compound of phosphorus and hydrogen, $P_2H_4$, which is spontaneously inflammable, and therefore the gas takes fire. If it is collected in a glass vessel over water, and allowed to stand so that the light acts upon it, the liquid phosphine is decomposed into the gaseous and solid varieties, and the gas which is left no longer has the property of tak-ing fire spontaneously. Phosphine is much less stable than ammonia. When heated or when treated with elec-tric sparks it is easily decomposed into phosphorus and hydrogen. While ammonia dissolves in water, probably forming the hydroxide $NH_4(OH)$, phosphine is only very slightly soluble in water. Ammonia combines with acids very energetically, forming the ammonium salts, and we should expect to find that similar salts are formed by the action of phosphine on acids; but only a few such compounds are known, and these are unstable. Thus, when phosphine is brought together with hydrochloric, hydrobromic, and hydriodic acids, the reactions repre-sented by the following equations take place:

$$PH_3 + HCl = PH_4Cl\ ;$$
$$PH_3 + HBr = PH_4Br\ ;$$
$$PH_3 + HI\ \ = PH_4I.$$

The products are called respectively *phosphonium chlo-ride, bromide*, and *iodide*. The reactions are, as will be

seen, perfectly analogous to those which take place between the same acids and ammonia. But the products are much less stable than the ammonium salts. The bromide when exposed to the air attracts water and decomposes rapidly, forming hydrobromic acid and phosphine. Phosphonium iodide undergoes a similar decomposition.

<div align="center">

ARSENIC, As (At. Wt. 74.44).

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**Occurrence.**—Arsenic occurs in nature to some extent in the uncombined condition or native. Compounds of the metals with arsenic, or the *arsenides*, occur very widely distributed, and they frequently accompany, and are similar to, the sulphides. The most common compound of this kind is the so-called *arsenical pyrites*, which has the composition FeAsS, and may therefore be regarded as iron pyrites, $FeS_2$, in which one atom of sulphur has been replaced by one atom of arsenic. Among other arsenic compounds deserving special mention are the two arsenides of iron of the formulas $FeAs_2$ and $Fe_2As_3$, which are apparently analogous to the sulphides $FeS_2$ and $Fe_2S_3$; and, further, the sulphides of arsenic, orpiment, $As_2S_3$, and realgar, $As_2S_2$. The oxide $As_2O_3$ occurs in considerable quantity, and also salts of arsenic acid, or the arsenates, which in composition are analogous to the phosphates.

**Preparation.**—The arsenic which comes into the market is either that which occurs native or it is made from arsenical pyrites by heating :

$$FeAsS = FeS + As.$$

The arsenic thus obtained is not pure. By bringing a little iodine in the bottom of a porcelain crucible, putting the arsenic upon it, and heating, the arsenic acquires a high metallic lustre, and once in this condition it will remain so for some time even when exposed to the air.

**Properties.**—Arsenic has a metallic lustre and steel color. It is very brittle. When heated it volatilizes

without melting. At red heat it burns with a bluish flame, and the vapor given off has the odor of garlic. This odor produced under such circumstances is very characteristic of arsenic, and furnishes one of the means for detecting it. Arsenic combines with most elements directly, the action being accompanied in some cases, as in that of chlorine, by an evolution of light. As an element it is not poisonous, but when oxidized to the form of the oxide $As_2O_3$ it is extremely poisonous. As it is easily oxidized, the element itself may act as a poison. When boiled with nitric acid arsenic is converted into arsenic acid, $H_3AsO_4$, just as phosphorus is converted by nitric acid into phosphoric acid, $H_3PO_4$.

One peculiarity in the conduct of arsenic is suggestive, and that is its power to form compounds which are analogous to the compounds of sulphur. There are a number of compounds similar to arsenical pyrites which appear to be perfectly analogous to the sulphur compounds, and in them it seems necessary to assume that the arsenic plays the same part as the sulphur. On the other hand, arsenic conducts itself in nearly all its compounds like phosphorus. This power to play double parts is not uncommon among the elements, and we shall hereafter meet with a number of examples. The case of manganese is one in point. While it conducts itself in some of its compounds like the members of the chlorine group, to which on account of its position in the periodic system we should expect to find it related, yet it is perhaps more closely related to iron and chromium, which belong to different groups; and so, also, chromium, which in many respects resembles sulphur very strikingly, is like iron and aluminium in other respects.

**Arsine, Arseniuretted Hydrogen, $AsH_3$.**—This compound is analogous to ammonia and to gaseous phosphine. It is made by reduction of compounds of arsenic containing oxygen, as arsenic trioxide or arsenic acid; and also by treating a compound of zinc and arsenic with dilute sulphuric acid. The reactions involved in the first method are

$$As_2O_3 + 6H_2 = 2AsH_3 + 3H_2O ;$$
$$H_3AsO_4 + 4H_2 = AsH_3 + 4H_2O.$$

That involved in the second method mentioned is:

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

Arsine is a colorless gas with an odor suggestive of garlic. It is extremely poisonous, even very small quantities being capable of producing bad effects, and it requires but little to cause death. When ignited in the air it takes fire and burns with a pale blue flame, the products of the combustion being arsenic trioxide, $As_2O_3$, and water. If the air is prevented from gaining free access to it the hydrogen burns, but the arsenic is deposited as a brownish layer. The gas is so unstable that, when it is passed through a glass tube heated to redness, it is decomposed into arsenic and hydrogen, the former being deposited just in front of the heated portion of the tube as a thin, almost black, layer with a high metallic lustre.

Arsine is easily decomposed by most active chemical substances. Water and concentrated acids decompose it; as do chlorine, bromine, and iodine, which form with it the corresponding acids, and compounds of chlorine, bromine, and iodine with arsenic.

Passed into a solution of a metallic salt, arsine either reduces the salt and throws down the metal as in the case of silver; or it forms an arsenide of the metal, acting in this case very much as hydrogen sulphide does when passed into similar solutions. Considering the instability of arsine, it is not surprising that it acts as a reducing agent. It will be remembered that hydriodic acid and hydrogen sulphide act in the same way towards some oxygen compounds, and the action is due to their breaking down into hydrogen and the other element. Thus, when hydriodic acid acts as a reducing agent the iodine is left uncombined, and when hydrogen sulphide acts in this way the sulphur is left. But when arsine acts as a reducing agent both the hydrogen and the arsenic com-

bine with oxygen. Thus, when arsine is passed into a solution of silver nitrate this reaction takes place :

$$AsH_3 + 6AgNO_3 + 3H_2O = As(OH)_3 + 6HNO_3 + 6Ag.$$

When, on the other hand, arsine is passed through a solution of a salt of a difficultly reducible metal, the arsenide of the metal is thrown down :

$$2AsH_3 + 3CuSO_4 = As_2Cu_3 + 3H_2SO_4.$$

Arsine does not combine with acids to form *arsonium* compounds such as $AsH_4I$, analogous to ammonium and phosphonium compounds.

There is a second compound of arsenic and hydrogen which is solid and appears to have the composition represented by the formula $As_2H_2$.

## ANTIMONY, Sb (At. Wt. 119.52).

**Occurrence.**—Antimony occurs in nature chiefly in the form of stibnite, which is the trisulphide $Sb_2S_3$. This also occurs very widely distributed in nature in combination with sulphides of various metals, as copper, lead, and silver. The element is made from the sulphide either by heating it with iron, with which the sulphur combines, leaving the antimony free ; or by roasting it, that is, heating it in combination with the air, thus converting the antimony into the tetroxide $Sb_2O_4$, and the sulphur into the dioxide $SO_2$, and then treating the oxide of antimony with reducing agents, as, for example, carbon :

$$Sb_2O_4 + 4C = 2Sb + 4CO.$$

**Properties.**—Antimony is hard and brittle ; has a silver-white color ; and a high metallic lustre. It can be distilled at white heat. At ordinary temperature it is not changed by contact with the air. When heated to a sufficiently high temperature in the air it takes fire and burns, forming the white oxide $Sb_2O_3$. It combines directly with chlorine, forming the chloride $SbCl_5$. Nitric acid oxidizes it either to antimony oxide, $Sb_2O_3$, or antimonic acid,

$H_3SbO_4$. *Aqua regia* dissolves it. Hot concentrated sulphuric acid dissolves it, forming antimony sulphate, and sulphur dioxide escapes. This action is similar to that which takes place when sulphuric acid acts upon copper. It is probable that the formation of the sulphur dioxide is due to the action of the hydrogen liberated from the sulphuric acid by the antimony in forming antimony sulphate:

$$2Sb + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2;$$
$$3H_2SO_4 + 3H_2 = 3SO_2 + 6H_2O.$$

This power to replace the hydrogen of some acids distinguishes antimony from arsenic and phosphorus, while its power to form acids corresponding to those of phosphorus and arsenic shows its analogy to these elements.

**Applications of Antimony.**—Antimony is used as a constituent of several alloys which are somewhat indefinite compounds which metallic elements form with one another. Among the alloys of antimony are type-metal, from which type is made, and britannia metal. The former consists of lead and antimony, and the latter of tin and antimony. There are a number of alloys which contain antimony which will be referred to under the other constituents.

**Stibine, $SbH_3$.**—This analogue of ammonia, phosphine, and arsine is more like arsine than it is like the others. It is made by the same methods as those used in making arsine, *i.e.*, by treating an alloy of zinc and antimony with sulphuric acid, or by reducing oxides of antimony by means of nascent hydrogen. The latter method gives a gas which contains a large percentage of hydrogen, but for most purposes this is not objectionable. It is only necessary to introduce into a flask containing zinc and dilute sulphuric acid a little of a solution of some oxygen compound of antimony, when the reduction is at once effected, and the escaping hydrogen contains stibine.

Stibine is a colorless, inodorous gas, which burns with a greenish-white flame. In general, it conducts itself much like arsine. It is unstable and breaks down when the tube through which it is passing is heated to red-

ness. It then leaves a deposit which looks like that formed in the case of arsine. When a cold object, as a piece of porcelain, is held for a moment in a flame of stibine a dark deposit is formed which resembles that formed with arsine.

**Methods of Distinguishing between Arsenic and Antimony.**—As arsenic is frequently used in cases of poisoning the question of deciding whether it is present in a given liquid or mixture is of great importance. One of the chief difficulties encountered is the similarity of the two elements arsenic and antimony. The method commonly employed in examining a substance for arsenic is known as *Marsh's test*. This consists in getting the substance in solution, and then pouring some of the liquid into a vessel containing pure zinc and pure dilute sulphuric acid. If arsenic is present in the solution it will, under these circumstances, be converted into arsine, the presence of which can be recognized by heating the tube through which the gas is passing, and by holding a piece of porcelain in the flame. If deposits are not formed in the tube or on the porcelain, arsenic is not present; but if deposits are formed, the only conclusion that can be drawn is that *either* arsenic *or* antimony is present, or possibly both may be present. For the purpose of distinguishing between the two elements, advantage is taken of the following differences between the spots : The antimony spots are darker than those formed by arsenic, and they have a smoky appearance, while those of arsenic have not; further, the arsenic deposits are quite volatile, and can therefore be driven before the flame in the tube or upon the porcelain, while those of antimony are not volatile; again, the deposits of arsenic are easily soluble in a solution of sodium hypochlorite or hypobromite, while the antimony deposits are insoluble in these solutions. There are other differences, but those mentioned will suffice to enable a careful worker and observer to distinguish between the two without any possibility of doubt. Another difficulty always encountered in examining for arsenic is the fact that the sulphuric acid, the zinc, and the glass of which the ves-

sels are made may contain arsenic. It is quite possible to overcome all the difficulties and to decide positively whether arsenic is present or not. If it is found that on heating the tube through which the hydrogen is passing no deposit is formed, even after continued heating, and that the hydrogen flame gives no deposit upon a piece of porcelain introduced into it, then it is safe to proceed with the examination of the suspected liquid. If the substance which is to be examined for arsenic has to be treated with chemical compounds in order to prepare it for analysis, every compound used in this part of the process must be separately examined for arsenic.

## BISMUTH, Bi (At. Wt. 206.54).

**Occurrence, etc.**—Bismuth is not abundant nor widely distributed in nature. It occurs for the most part native in veins of granite and clay slate. Among the compounds of bismuth found in nature are the oxide $Bi_2O_3$ and the corresponding sulphide $Bi_2S_3$.

The ores are roasted and then treated with appropriate reducing agents. In different places different methods of extraction are employed. As the chief applications of bismuth are for pharmaceutical purposes, it is necessary that the element should be specially pure; above all, that it should not be contaminated with arsenic. In order to remove the last traces of this element the powdered bismuth is generally melted with saltpeter.

Bismuth is a hard, brittle, reddish-white substance with a metallic lustre. It looks very much like antimony, but is distinguished from it by its reddish tint. At ordinary temperatures it remains unchanged in the air. When heated to red heat it burns with a bluish flame, forming the yellow oxide $Bi_2O_3$.

Hydrochloric acid scarcely acts upon it; concentrated sulphuric acid forms *bismuth sulphate*, $Bi_2(SO_4)_3$, in which the bismuth evidently plays the part of a base-forming element; nitric acid gives *bismuth nitrate*, $Bi(NO_3)_3$, which is partly decomposed by water, forming so-called basic nitrates which are difficultly soluble in water. These salts will be taken up in the next chapter.

Some bismuth is used in the preparation of alloys which are easily fusible, as, for example, Newton's metal, which contains bismuth, lead, and tin; Rose's metal, which consists of the same constituents in slightly different proportions; and Wood's metal, which consists of bismuth, lead, tin, and cadmium.

Bismuth does not combine with hydrogen.

**Compounds of the Members of the Phosphorus Group with the Members of the Chlorine Group.**—In the introduction to this chapter it was stated that the elements of the phosphorus group combine with chlorine in two proportions, forming compounds of the general formulas $MCl_3$ and $MCl_5$. Arsenic, however, forms only one compound with chlorine, $AsCl_3$, while bismuth forms one of the formula $BiCl_3$, and another, $Bi_2Cl_4$. The compounds of phosphorus and chlorine are the best known, and a brief study of these will give a fair idea of the methods of preparation and the conduct of the analogous compounds of the other members of the group.

**Phosphorus Trichloride, $PCl_3$,** is made by conducting dry chlorine gas upon phosphorus in a retort connected with a receiver. Action takes place at once with evolution of heat, and the trichloride distils over and is condensed as a liquid into the receiver. It is purified by distillation on a water-bath. It is a clear, colorless liquid, which boils at 74°. In contact with air it fumes in consequence of the action of the water vapor which decomposes it. It has a disagreeable odor of its own mixed with that of hydrochloric acid. Its most characteristic decomposition is that which it undergoes with water, which is of the same kind as that which the chlorides of sulphur, selenium, and tellurium undergo with water. The general tendency of the chlorides of the acid-forming elements is to undergo decomposition with water in such a way that the corresponding hydroxyl compound is formed, together with hydrochloric acid. This is shown in the case of tellurium tetrachloride, which with water forms normal tellurious acid, $Te(OH)_4$, and hydrochloric acid :

$$\text{TeCl}_4 + \begin{array}{l} \text{HOH} \\ \text{HOH} \\ \text{HOH} \\ \text{HOH} \end{array} = \text{Te} \left\{ \begin{array}{l} \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \right. + 4\text{HCl}.$$

In the case of sulphur tetrachloride the hydroxyl derivative, if formed, breaks down into water and sulphur dioxide. When phosphorus trichloride is treated with water the decomposition is probably represented by the equation

$$\text{PCl}_3 + \begin{array}{l} \text{HOH} \\ \text{HOH} \\ \text{HOH} \end{array} = \text{P} \left\{ \begin{array}{l} \text{OH} \\ \text{OH} \\ \text{OH} \end{array} \right. + 3\text{HCl}.$$

From some experiments it appears possible that this form of compound is unstable, and that, owing to the marked tendency of phosphorus to act as a quinquivalent element, the constituents arrange themselves differently, as represented in the formula $\text{O}=\text{P} \left\{ \begin{array}{l} \text{H} \\ \text{OH} \\ \text{OH} \end{array} \right.$. This question will be referred to under the head of Phosphorous Acid.

The trichloride shows a strong tendency to take up chlorine, bromine, iodine, oxygen, and sulphur, and thus to become saturated as a quinquivalent element. With chlorine it forms the pentachloride, $\text{PCl}_5$, with oxygen the oxychloride, $\text{POCl}_3$, and with sulphur the sulphochloride, $\text{PSCl}_3$. It does not, however, readily take up free oxygen or free sulphur directly, but will take up these elements from compounds in which they are not firmly held. Thus, when the trichloride is brought together with sulphur trioxide this reaction takes place:

$$\text{SO}_3 + \text{PCl}_3 = \text{POCl}_3 + \text{SO}_2 ;$$

and when it is brought together with a polysulphide, as $\text{Na}_2\text{S}_5$, it takes up a part of the sulphur and forms the sulphochloride, $\text{PSCl}_3$. So, further, it is converted into the oxychloride when treated with ozone. These reactions show the marked tendency which the trichlo-

ride has to pass over into compounds of quinquivalent phosphorus—a tendency which is characteristic of phosphorus compounds in general.

**Phosphorus Pentachloride, PCl₅**, is formed by treating phosphorus or the trichloride with dry chlorine. It is best prepared by passing chlorine through a wide tube upon the surface of the trichloride, contained in a vessel, which is kept cool. Gradually the liquid becomes thicker and thicker, and finally, if well stirred, it becomes solid. It is a white solid, but it generally has a slightly yellowish or greenish color in consequence of a slight decomposition into the trichloride and free chlorine. It sublimes below 100° without melting. When heated to boiling it undergoes partial decomposition into chlorine and the trichloride, and this decomposition is complete at about 300°. As the temperature is raised from the apparent boiling point to the point at which the decomposition is complete, the color of the vapor is seen to grow darker in consequence of the increased quantity of free chlorine present. The decomposition is gradual, and, for any given temperature, the amount of decomposition is constant. This kind of decomposition, which is known as *dissociation*, has been studied very carefully, and is found to be capable of explanation by the aid of the kinetic theory of gases. In a later chapter this subject will be treated, and a number of other examples will be given. Owing to this decomposition under the influence of heat the specific gravity of the vapor of phosphorus pentachloride is not what it should be, if the formula is $PCl_5$. On the other hand, the specific gravity of the vapor of the trichloride leads to the formula $PCl_3$, and that of the oxychloride to the formula $POCl_3$. The apparent anomaly presented by the pentachloride is easily understood. When a molecule of the compound is converted into vapor, or is heated to a sufficiently high temperature, it is broken down in accordance with this equation :

$$PCl_5 = PCl_3 + Cl_2.$$

From the one molecule, therefore, two gaseous molecules are obtained. Consequently the vapor formed occupies twice as much space as it would if there were no decomposition. It follows that the specific gravity of the vapor must be only half what it would be if there were no decomposition. When the compound is converted into vapor in an atmosphere of phosphorus trichloride, the decomposition referred to does not take place, and, under these circumstances, the specific gravity is found to be in accordance with Avogadro's law, and with the formula $PCl_5$. This case is a particularly interesting one, as it has played an important part in the discussions in regard to the validity of Avogadro's law.

The conduct of phosphorus pentachloride towards water is in general like that of the other chlorides of acid-forming elements. But, owing probably to a secondary action, the product is not the corresponding hydroxyl compound. It is probable that the first action of the water is represented by the equation

$$PCl_5 + \frac{HHO}{HHO} = P \begin{cases} OH \\ OH \\ Cl_3 \end{cases} + 2HCl.$$

But this product, if formed, breaks down at once into phosphorus oxychloride and water, and the water thus given off acts upon a further quantity of the pentachloride :

$$P \begin{cases} OH \\ OH \\ Cl_3 \end{cases} = P \begin{cases} O \\ Cl_3 \end{cases} + H_2O.$$

The formation of the oxychloride from the pentachloride by the action of water takes place very easily. The oxychloride is then further acted upon by the water, and each chlorine atom is replaced by hydroxyl :

$$OPCl_3 + \begin{matrix} HOH \\ HOH \\ HOH \end{matrix} = OP \begin{cases} OH \\ OH \\ OH \end{cases} + 3HCl.$$

The final product is the acid $H_3PO_4$, or phosphoric acid.

It will be seen that the effect of phosphorus pentachloride upon water is to replace the hydroxyl of the water by chlorine. Thus, one molecule of the pentachloride and five molecules of water give one molecule of phosphoric acid and five of hydrochloric acid:

$$PCl_5 + \begin{matrix} HOH \\ HOH \\ HOH \\ HOH \\ HOH \end{matrix} = OP(OH)_3 + \begin{matrix} HCl \\ HCl \\ HCl \\ HCl \\ HCl \end{matrix} + H_2O.$$

In the reaction, the hydroxyl of the water and the chlorine of the chloride exchange places. Similarly, when any compound which contains hydroxyl is treated with phosphorus pentachloride the same reaction takes place, the hydroxyl being replaced by chlorine. Therefore phosphorus pentachloride may be used as a reagent for testing for the hydroxyl condition in compounds. If a compound which contains hydrogen and oxygen is treated with the pentachloride, and an atom of hydrogen and one of oxygen is replaced by an atom of chlorine, the conclusion is drawn that the compound contains hydroxyl. This, of course, amounts to saying that the compound resembles water in its reaction with the pentachloride, and this is most easily explained by the assumption that the same condition exists in both. It should be borne in mind, further, that, in general, any compound of chlorine with an acid-forming element which undergoes decomposition with water might be used for the same purpose. The action of the pentachloride upon a hydroxyl compound is well illustrated in the case of sulphuric acid:

$$SO_2{<}^{OH}_{OH} + PCl_5 = POCl_3 + SO_2{<}^{Cl}_{OH} + HCl.$$

The action of the oxychloride would take place as represented thus:

$$3SO_2{<}^{OH}_{OH} + POCl_3 = PO(OH)_3 + 3SO_2{<}^{Cl}_{OH}.$$

Phosphorus forms a tribromide, $PBr_3$, and a penta-bromide, $PBr_5$, similar to the chlorides. With iodine it forms the compounds $P_2I_4$ and $PI_3$, and with fluorine a trifluoride, $PF_3$, and a pentafluoride, $PF_5$.

**Arsenic Trichloride, $AsCl_3$,** is the only compound which arsenic forms with chlorine. It is easily made by passing chlorine into a retort containing powdered arsenic. It is also formed by the action of phosphorus pentachloride on arsenic trioxide, in which case the oxygen of the trioxide is simply replaced by chlorine:

$$As_2O_3 + 3PCl_5 = 3POCl_3 + 2AsCl_3.$$

Further, it is obtained when dry hydrochloric acid gas is passed over arsenic trioxide, and it is present in solution when the trioxide is dissolved in strong hydrochloric acid.

Arsenic trichloride is a liquid which boils at about 134°. It is extremely poisonous. If a hydrochloric acid solution of the trichloride is boiled, it passes over when the temperature rises above 100°. When substances containing arsenic are heated in a retort with sulphuric acid and sodium chloride, arsenic chloride is formed and passes over into the receiver.

When arsenic trichloride is treated with a little water two of the chlorine atoms are replaced by hydroxyl, thus:

$$As\begin{Bmatrix} Cl \\ Cl \\ Cl \end{Bmatrix} + \begin{matrix} HOH \\ HOH \end{matrix} = As\begin{Bmatrix} OH \\ OH \\ Cl \end{Bmatrix} + 2HCl.$$

If treated with much water it yields arsenious acid :

$$AsCl_3 + 3H_2O = As(OH)_3 + 3HCl.$$

We have here a curious illustration of the effect of the relative quantities of the substances which take part in a reaction upon the nature of the reaction. When

arsenic trioxide is treated with an excess of hydrochloric acid it is converted into the chloride:

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

If, on the other hand, the chloride is treated with a large excess of water it is completely broken down, yielding the trihydroxyl derivative, or arsenious acid. There are many other illustrations of this kind met with among chemical reactions, and the subject of the influence of mass in determining the character of a reaction has been studied with much care. This subject will receive attention in a later chapter under the head of Mass Action.

**Compounds of Antimony and Chlorine.**—Antimony forms two compounds with chlorine, analogous in composition to the two chlorides of phosphorus. These are *antimony trichloride*, $SbCl_3$, and *antimony pentachloride*, $SbCl_5$. The trichloride is formed by direct treatment of the element with chlorine. It is also formed by dissolving antimony in hydrochloric acid with addition of nitric acid, and when this solution is distilled the chloride of antimony passes over. At the ordinary temperatures it is a solid, colorless, crystalline, soft substance, which, on account of its consistency, has received the common name "butter of antimony" (*Butyrum Antimonii*). When treated with water it forms an oxychloride, the composition of which varies according to circumstances, but it generally approximates to that represented by the formula $Sb_4O_5Cl_2$. If treated with cold water the decomposition is simple, the product being antimony oxychloride, $SbOCl$:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

The oxychlorides formed by treating antimony trichloride with hot water, which, as already stated, have a composition approximating that represented by the formula $Sb_4O_5Cl_2$, are known as "*Powder of Algaroth*." The relation of this compound to the simple oxychloride, $SbOCl$, is indicated by the equation

$$5SbOCl = Sb_4O_5Cl_2 + SbCl_3.$$

*Liquor Stibii Muriatici* is a solution of antimony tri-chloride prepared by dissolving antimony sulphide in concentrated hydrochloric acid:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Antimony chloride has a caustic action and is used in medicine. It is also used for the purpose of burnishing iron ware, as gun-barrels. When treated with the chloride they acquire a brownish, bronze-like color.

*Pentachloride of Antimony* is in general like the pentachloride of phosphorus. It gives up its chlorine, however, somewhat more readily. When treated with water it yields first an oxychloride, $SbO_2Cl$, and this is further acted upon and converted into antimonic acid, $H_3SbO_4$.

**Bismuth and Chlorine.**—Bismuth differs from the other members of the phosphorus group in its conduct towards chlorine. It forms the chloride, $Bi_2Cl_4$, of which there is no analogue among the compounds of the other elements of the group with chlorine. The compound may, however, be regarded as analogous to the hydrogen compounds hydrazine, $N_2H_4$, and liquid phosphine, $P_2H_4$. *Bismuth dichloride,* $Bi_2Cl_4$, is formed by reduction of the trichloride, $BiCl_3$, when the latter is treated with hydrogen at a temperature of about $300°$. *Bismuth trichloride,* $BiCl_3$, is formed by treating bismuth with chlorine, and by dissolving bismuth oxide, $Bi_2O_3$, in hydrochloric acid. From this solution a crystallized compound of the formula $BiCl_3 + H_2O$ is deposited, and it is impossible to drive all the water off from this compound without causing decomposition. Treated with water the chloride is decomposed, forming the oxychloride, $BiOCl$:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

**Double Salts.**—When the chlorides, bromides, iodides, and fluorides of the members of the phosphorus group are treated with the corresponding salts of potassium, sodium,

and some other strongly marked base-forming elements, compounds known as double salts are formed. Thus, when antimony trichloride is treated with a strong water solution of potassium chloride, a salt of the composition $SbCl_3.3KCl$ is formed. This compound appears to be analogous to the oxygen compound $K_3SbO_3$, or potassium antimonite, differing from it in containing chlorine in place of the oxygen. While the latter is derived from an acid of the composition $H_3SbO_3$, the former appears to be derived from the corresponding chlorine acid, $H_3SbCl_6$. Similar compounds of sulphur and tellurium are known, and one was referred to on page 205. This is the potassium compound $K_2TeBr_6$ or $TeBr_4.2KBr$, which, as explained there, is analogous to potassium tellurite, $K_2TeO_3$.

# CHAPTER XVIII.

**Introduction.**—The product of the direct action of oxygen upon phosphorus is the pentoxide $P_2O_5$. Arsenic, antimony, and bismuth, however, form the trioxides $As_2O_3$, $Sb_2O_3$, and $Bi_2O_3$. It is possible to obtain a compound of arsenic and oxygen of the formula $As_2O_5$, one of antimony, $Sb_2O_4$, and another, $Sb_2O_5$, and, finally, two oxides of bismuth, $Bi_2O_2$ and $Bi_2O_5$. Phosphorus, further, forms the oxides $P_4O$, $P_2O_3$, and $P_2O_4$. The table below contains the formulas of the above-mentioned compounds systematically arranged:

| | | | |
|---|---|---|---|
| $P_4O$ | —— | —— | $Bi_2O_2$ |
| $P_2O_3$ | $As_2O_3$ | $Sb_2O_3$ | $Bi_2O_3$ |
| $P_2O_4$ | —— | $Sb_2O_4$ | —— |
| $P_2O_5$ | $As_2O_5$ | $Sb_2O_5$ | $Bi_2O_5$ |

The final products of the oxidation of the elements of this group, if water is present, are phosphoric, arsenic, antimonic, and bismuthic acids. All of these are well-marked acids except the last. They can all be regarded as derived from the normal acids of the general formula $M(OH)_5$ by loss of one or two molecules of water. The common forms of phosphoric, arsenic, and antimonic acids are those which are formed from the normal acids by loss of one molecule of water:

$$P(OH)_5 \quad = \quad P\left\{ \begin{array}{l} O \\ (OH)_3 \end{array} \right. \quad + \quad H_2O;$$

Normal phosphoric acid     Orthophosphoric acid

$$As(OH)_5 \quad = \quad As\left\{ \begin{array}{l} O \\ (OH)_3 \end{array} \right. \quad + \quad H_2O;$$

Normal arsenic acid     Orthoarsenic acid

(321)

$$\text{Sb(OH)}_5 \quad = \quad \text{Sb} \begin{cases} \text{O} \\ \text{(OH)}_3 \end{cases} \quad + \quad \text{H}_2\text{O.}$$

Normal antimonic acid     Orthoantimonic acid

Bismuthic acid appears, however, to be formed from the normal acid by loss of two molecules of water, just as the so-called *metaphosphoric, metarsenic,* and *metantimonic* acids are:

$$\text{Bi(OH)}_5 \quad = \quad \text{Bi} \begin{cases} \text{O}_2 \\ \text{OH} \end{cases} \quad + \quad 2\text{H}_2\text{O};$$

Normal bismuthic acid     Bismuthic acid

$$\text{P(OH)}_5 \quad = \quad \text{P} \begin{cases} \text{O}_2 \\ \text{OH} \end{cases} \quad + \quad 2\text{H}_2\text{O};$$

Metaphosphoric acid

$$\text{As(OH)}_5 \quad = \quad \text{As} \begin{cases} \text{O}_2 \\ \text{OH} \end{cases} \quad + \quad 2\text{H}_2\text{O};$$

Metarsenic acid

$$\text{Sb(OH)}_5 \quad = \quad \text{Sb} \begin{cases} \text{O}_2 \\ \text{OH} \end{cases} \quad + \quad 2\text{H}_2\text{O.}$$

Metantimonic acid

From the ordinary or *ortho acids,* and from the *meta acids,* more complex forms can be derived by loss of different quantities of water. The most common form besides those mentioned is that seen in the so-called *pyro acids,* of which pyrophosphoric acid is the best known example. It is formed from the ortho acid by loss of one molecule of water from two molecules of the acid, just as pyrosulphuric or disulphuric acid is formed from two molecules of ordinary sulphuric acid by loss of one molecule of water. The formation of pyrophosphoric acid from orthophosphoric acid takes place according to the equation

$$\text{P} \begin{cases} \text{O} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} \quad = \quad \text{P} \begin{cases} \text{O} \\ \text{OH} \\ \text{OH} \\ \text{O} \end{cases} \quad + \quad \text{H}_2\text{O};$$
$$\text{P} \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{O} \end{cases} \quad\quad\quad \text{P} \begin{cases} \text{OH} \\ \text{OH} \\ \text{O} \end{cases}$$

or

$$2H_3PO_4 \quad = \quad H_4P_2O_7 \quad + \quad H_2O.$$

Orthophosphoric acid        Pyrophosphoric acid

Pyroarsenic and pyroantimonic acids bear the same relations to the ortho acids that pyrophosphoric acid bears to orthophosphoric acid.

By partial oxidation of phosphorus in presence of water, phosphorous acid, $H_3PO_3$, is formed. The same acid is formed by the action of phosphorus trichloride on water. According to the latter method of formation we should expect to find that this acid is normal phosphorous acid, $P(OH)_3$. As already stated, however, it appears probable that the acid has the constitution

$$O=P{\overset{\displaystyle H}{\underset{\displaystyle OH}{\big\langle}}}OH.$$ The acids of arsenic and antimony of

similar composition seem to be the normal acids $As(OH)_3$ and $Sb(OH)_3$. The hydroxyl derivative of bismuth corresponding to these acids has no acid properties, but on the contrary is basic. Hypophosphorous acid has the composition $H_3PO_2$. It is monobasic, and it appears therefore that it contains but one hydroxyl, as represented in the formula $H_2OP(OH)$. It is possible that the relations between phosphoric, phosphorous, and hypophosphorous acids should be represented by the formulas

$$OP\left\{\begin{array}{l} OH \\ OH, \\ OH \end{array}\right. \qquad OP\left\{\begin{array}{l} H \\ OH, \\ OH \end{array}\right. \qquad OP\left\{\begin{array}{l} H \\ H \\ OH \end{array}\right. .$$

Phosphoric acid        Phosphorous acid        Hypophosphorous acid

The fundamental compound, then, from which these may be regarded as derived is the unknown oxyphosphine $OPH_3$. By oxidation we should expect phosphine to yield in successive stages the three products above named:

$$P\left\{\begin{array}{l} H \\ H \\ H \end{array}\right. , \; OP\left\{\begin{array}{l} H \\ H \\ H \end{array}\right. , \; OP\left\{\begin{array}{l} H \\ H \\ OH \end{array}\right. , \; OP\left\{\begin{array}{l} H \\ OH \\ OH \end{array}\right. , \; OP\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right. .$$

Unknown        Hypophosphorous        Phosphorous        Phosphoric
                        acid                acid                acid

The oxidation of hydrogen sulphide takes place sim‑
ilarly, as has been shown:

$$S \begin{cases} H \\ H \end{cases}, \qquad O_2S \begin{cases} H \\ H \end{cases}, \qquad O_2S \begin{cases} H \\ OH \end{cases}, \qquad O_2S \begin{cases} OH \\ OH \end{cases}.$$

<center>Unknown      Sulphurous acid      Sulphuric acid</center>

With oxygen and chlorine the elements of the phos‑
phorus group form a number of compounds known as
oxychlorides. Towards chlorine as well as towards
oxygen all these elements except bismuth are quin‑
quivalent. A part or all of the oxygen of the oxygen
compounds can be replaced by chlorine. Starting with
the chlorine compound on the one hand, oxychlorides
can be obtained from it, until all the chlorine is replaced
by oxygen, and the limit is reached in the oxide. So
also the chlorine can be replaced by hydroxyl and the
acids thus obtained.

(1) $PCl_5$ gives $POCl_3$ and $P_2O_5$ as final product;
(2) $PCl_5$ gives $POCl_3$ and with water $PO(OH)_3$.
(3) $PCl_3$ gives as final product $P_2O_3$;
(4) $PCl_3$ gives with water $P(OH)_3$.

Intermediate products are supposable, but not known,
as, for example:

$$P \begin{cases} Cl \\ Cl \\ Cl \end{cases} \qquad P \begin{cases} Cl \\ Cl \\ OH \end{cases}, \qquad P \begin{cases} Cl \\ OH \\ OH \end{cases}, \qquad P \begin{cases} OH \\ OH \\ OH \end{cases}.$$

A compound of arsenic of the formula $As \begin{cases} Cl \\ (OH)_2 \end{cases}$ is
known, however, and this plainly corresponds to one of
these intermediate products.

With sulphur phosphorus apparently forms a large
number of compounds. Among them are two which
have the formulas $P_2S_3$ and $P_2S_5$. These plainly are
analogous to the two oxides of phosphorus, $P_2O_3$ and
$P_2O_5$. When treated with water these sulphur com‑
pounds like the corresponding chlorine compounds
yield the oxygen acids. Thus the trisulphide undergoes

decomposition with water according to the following equation:

$$P_2S_3 + 6H_2O = 2H_3PO_3 + 3H_2S;$$

and the pentasulphide is converted by water into phosphoric acid:

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

Arsenic forms with sulphur several compounds, the principal of which are the *disulphide*, $As_2S_2$, the *trisulphide*, $As_2S_3$, and the *pentasulphide*, $As_2S_5$. The principal sulphides of antimony are those of the formulas $Sb_2S_3$ and $Sb_2S_5$, and of bismuth those of the formulas $Bi_2S_2$ and $Bi_2S_3$. In general, therefore, the sulphur compounds are analogous in composition to the oxygen compounds, while the number of sulphur compounds of these elements is larger than that of the oxygen compounds. The formulas of the principal sulphur compounds of this group are given systematically arranged in the table below:

|  | $As_2S_2$ |  | $Bi_2S_2$ |
|---|---|---|---|
| $P_2S_3$ | $As_2S_3$ | $Sb_2S_3$ | $Bi_2S_3$ |
| $P_2S_5$ | $As_2S_5$ | $Sb_2S_5$ |  |

Further, there are sulphur acids which are to be regarded as the oxygen acids, a part or all of whose oxygen is replaced by sulphur. Thus, in the case of arsenic the following possibilities suggest themselves, starting with arsenious acid:

$$As\begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix},\ As\begin{Bmatrix} OH \\ OH \\ SH \end{Bmatrix},\ As\begin{Bmatrix} OH \\ SH \\ SH \end{Bmatrix},\ As\begin{Bmatrix} SH \\ SH \\ SH \end{Bmatrix};$$

and starting with arsenic acid, the following possibilities suggest themselves:

$$OAs\begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix},\ SAs\begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix},\ SAs\begin{Bmatrix} OH \\ OH \\ SH \end{Bmatrix},\ SAs\begin{Bmatrix} OH \\ SH \\ SH \end{Bmatrix},\ SAs\begin{Bmatrix} SH \\ SH \\ SH \end{Bmatrix}.$$

While none of these compounds is known, many com-
pounds are known which are to be regarded as salts of
one or another of these acids. Thus salts of the general
formulas $M_2AsS_3$ and $M_3AsS_4$ are well known, as are also
salts of the general formula $MAsS_2$, which are derived
from the acid $As \begin{cases} S \\ SH \end{cases}$, corresponding to the oxygen
compound $As \begin{cases} O \\ OH \end{cases}$, which in turn is derived from arsen-
ious acid by loss of one molecule of water:

$$As \begin{cases} OH \\ OH \\ OH \end{cases} = As \begin{cases} O \\ OH \end{cases} + H_2O.$$

So, too, we have :

$$As \begin{cases} SH \\ SH \\ SH \end{cases} = As \begin{cases} S \\ SH \end{cases} + H_2S.$$

Similar compounds of antimony are also well known.
The possibility of making analogous compounds contain-
ing selenium and tellurium will suggest itself.

**Phosphoric Acid, Orthophosphoric Acid, $H_3PO_4$.**—The
compound to which the name phosphoric acid is gener-
ally applied, and from which the best known phosphates
are derived, is that which has the formula $H_3PO_4$. To
distinguish it from the other varieties it is called *ortho-
phosphoric acid.* As has been stated, this is the final
product of oxidation of phosphorus in the presence of
water. Thus, when phosphorus is boiled with nitric acid
it is converted into orthophosphoric acid ; and also when
phosphorus is burned in the air, and the product dis-
solved in water, phosphoric acid is formed. In this case
the first product of the oxidation is the pentoxide $P_2O_5$,
also known as phosphoric anhydride, and when this is
treated with water it is converted into phosphoric acid :

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The occurrence of phosphoric acid in nature has already

been referred to in connection with the occurrence of phosphorus, which is found in nature almost exclusively in the form of phosphates, principally as calcium phosphate, $Ca_3(PO_4)_2$, in phosphorite, apatite, and the ashes of bones. It is formed when either phosphorus pentachloride or the oxychloride is decomposed by water:

$$PCl_5 + 4H_2O = PO(OH)_3 + 5HCl;$$
$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl;$$

and from the analogous bromine and iodine compounds in the same way. In order to prepare the acid two ways suggest themselves: (1) by oxidizing phosphorus with nitric acid; and (2) by extracting it from one of the natural phosphates, as phosphorite or bone-ash. The first of these methods is better adapted to the preparation of pure phosphoric acid, such as is needed for medicinal purposes; the latter is used where absolute purity of the product is not required. It should be said, however, that the acid obtained by oxidation of phosphorus is not pure, as commercial phosphorus almost always contains arsenic and small quantities of other impurities. The arsenic can easily be removed by passing hydrogen sulphide through the solution after the nitric acid has been evaporated. If the solution is then filtered and evaporated to dryness, the orthophosphoric acid is transformed into pyrophosphoric or metaphosphoric acid according to the temperature:

$$2H_3PO_4 = H_4P_2O_7 + H_2O;$$
$$H_3PO_4 = HPO_3 + H_2O.$$

The preparation of phosphoric acid from a phosphate is not a simple matter. If the acid were volatile or insoluble there would be no difficulty in separating it. In the former case it would only be necessary to proceed as in preparing hydrochloric and nitric acids. By adding an acid which is not volatile except at a high temperature, such, for example, as sulphuric acid, and heating, the non-volatile acid replaces the volatile. On the other

hand, if phosphoric acid were insoluble in water, it could be separated by adding a soluble acid to one of its soluble salts. When, for example, nitric acid is added to a solution of potassium tellurite, $K_2TeO_3$, tellurious acid, being insoluble, is thrown down :

$$K_2TeO_3 + 2HNO_3 = 2KNO_3 + H_2TeO_3.$$

But phosphoric acid is not volatile and is soluble, so that plainly neither of these methods can be used. By treating the calcium salt with sulphuric acid the calcium can be completely separated in the form of calcium sulphate, which is difficultly soluble in water and insoluble in alcohol. The ideal reaction to be accomplished is that represented in the following equation :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

But when sulphuric acid is added to calcium phosphate, only a part of the calcium is thrown down as sulphate, the rest remaining in the form of primary calcium phosphate :

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The phosphate thus formed is soluble in water, and the calcium is not easily precipitated from it. By evaporation and addition of sufficient sulphuric acid and alcohol the precipitation can be effected, and a solution of phosphoric acid thus obtained. This acid is not pure, as there are substances in bone-ash which are not removed by the method described.

Phosphoric acid for medicinal purposes is often made by dissolving the pentoxide in water.

**Properties.**—When evaporated to the proper consistency the acid forms a thick syrup which slowly solidifies in the form of large crystals. The crystals are deliquescent. When heated to a sufficiently high temperature the acid loses water, as already explained, and yields, first, pyrophosphoric, and then metaphosphoric acid. It is a tribasic acid, capable of yielding three classes of

salts of the general formulas $OP \begin{cases} OH \\ OH \\ OM \end{cases}$, $OP \begin{cases} OH \\ OM \\ OM \end{cases}$, and

$OP \begin{cases} OM \\ OM \\ OM \end{cases}$, which are known respectively as the *primary*,

*secondary*, and *tertiary phosphates*. The primary and secondary phosphates are also known as *acid phosphates*, and the tertiary salts as *neutral* or *normal phosphates*. In these salts it is not necessary that all the hydrogen should be replaced by the same metal. There are salts in which two or three metals take the place of the hydrogen atoms. A phosphate much used in the laboratory, for example, is one in which one hydrogen atom of phosphoric acid is replaced by a sodium atom, and another by the ammonium group, $NH_4$. This salt has the formula $OP \begin{cases} OH \\ ONa \\ ONH_4 \end{cases}$,

and is called *ammonium sodium phosphate*. Another phosphate commonly met with is *ammonium magnesium phosphate*, $OP \begin{cases} ONH_4 \\ O \\ O \end{cases} > Mg$, which is derived from the acid

by replacement of two hydrogen atoms in the molecule by one bivalent magnesium atom, and one by the ammonium group. The changes which these three classes of phosphates undergo when heated are of special interest. The tertiary phosphates are stable. The primary and secondary phosphates give up all their hydrogen, which passes off in the form of water. Thus, primary sodium phosphate, $H_2NaPO_4$, loses one molecule of water from each molecule of the salt, and is converted into the *metaphosphate*, $NaPO_3$:

$$OP \begin{cases} OH \\ OH \\ ONa \end{cases} = O_2P(ONa) + H_2O.$$

In general, *the primary phosphates are converted into metaphosphates by heat.*

When a secondary phosphate is heated the product is

a pyrophosphate, as when secondary sodium phosphate is heated to a sufficiently high temperature it is converted into sodium pyrophosphate :

$$\mathrm{OP}\begin{cases}\mathrm{ONa}\\ \mathrm{ONa}\\ \mathrm{OH}\end{cases} \quad \mathrm{OP}\begin{cases}\mathrm{ONa}\\ \mathrm{ONa}\\ \mathrm{O}\end{cases}$$
$$\mathrm{OP}\begin{cases}\mathrm{OH}\\ \mathrm{ONa}\\ \mathrm{ONa}\end{cases} = \quad \mathrm{OP}\begin{cases}\mathrm{ONa}\\ \mathrm{ONa}\end{cases} + \mathrm{H_2O}.$$

In general, *a secondary phosphate is converted into a pyrophosphate by heat.*

The above rules do not hold good for ammonium salts, for these always undergo another kind of decomposition when heated. When sodium ammonium phosphate is heated, ammonia is first given off, thus :

$$\mathrm{HNa(NH_4)PO_4 = H_2NaPO_4 + NH_3};$$

and the primary salt formed breaks down according to the above rule, forming the metaphosphate. So, also, when ammonium magnesium phosphate is heated, the first change consists in the giving off of ammonia, thus .

$$\mathrm{(NH_4)MgPO_4 = HMgPO_4 + NH_3};$$

and the secondary magnesium phosphate thus formed then breaks down, forming the pyrophosphate, $\mathrm{Mg_2P_2O_7}$ :

$$\mathrm{2HMgPO_4 = Mg_2P_2O_7 + H_2O}.$$

The presence of phosphoric acid can be detected by means of the following characteristic reactions : With silver nitrate it gives a yellow precipitate of tertiary silver phosphate, $\mathrm{Ag_3PO_4}$ ; with a soluble magnesium salt and ammonia it gives ammonium magnesium phosphate, $\mathrm{(NH_4)MgPO_4}$, which is insoluble in water ; with a solution of ammonium molybdate, $\mathrm{(NH_4)_2MoO_4}$, which contains nitric acid, it gives a complicated insoluble salt, ammonium phospho-molybdate (which see).

**Pyrophosphoric Acid, $\mathrm{H_4P_2O_7}$.**—When phosphoric acid is heated to 200°–300° until a specimen neutralized with ammonia gives a pure white precipitate with silver nitrate, it is completely transformed into pyrophosphoric acid by

loss of water. The white precipitate referred to is the silver salt of pyrophosphoric acid. The silver salt of orthophosphoric acid is yellow. This difference in color led, many years ago, to a careful investigation of the change in composition which phosphoric acid undergoes when heated, and to the recognition of the existence of pyrophosphoric acid as distinct from orthophosphoric acid; and the study of the relations existing between these acids and metaphosphoric acid has had a strong influence in shaping the views of chemists in regard to the relations between other similar acids. The views at present held in regard to the relations between the common forms of oxygen acids and the so-called normal acids or maximum hydroxides are simply an extension of the ideas first introduced into chemistry in connection with the three varieties of phosphoric acid. The different varieties of periodic acid, and the modifications of sulphuric acid seen in the normal acid, $S(OH)_6$, the ordinary acid, $SO_2(OH)_2$, and the pyro-acid, $H_2S_2O_7$, are examples of the same kind of relations.

*Pyrophosphates* are formed, as we have seen, when the secondary phosphates, like disodium phosphate, $HNa_2PO_4$, are heated.

**Metaphosphoric Acid, $HPO_3$.**—This acid is formed by dissolving phosphorus pentoxide, $P_2O_5$, in cold water:

$$P_2O_5 + H_2O = 2HPO_3.$$

It is also formed by heating phosphoric acid to 400°:

$$H_3PO_4 = HPO_3 + H_2O.$$

Further, the metaphosphates are formed by heating the primary phosphates like primary sodium phosphate, $H_2NaPO_4$. The acid is a vitreous translucent mass, known in the market as *glacial phosphoric acid* (*Acidum phosphoricum glaciale*). It is the more common commercial form of phosphoric acid. It is a monobasic acid, and in composition is analogous to nitric and chloric acids:

$HPO_3$, . . . . . Metaphosphoric acid.
$HNO_3$, . . . . . Nitric acid.
$HClO_3$, . . . . . Chloric acid.

When boiled with water in which there is a little nitric acid metaphosphoric acid is readily converted into orthophosphoric acid:

$$HPO_3 + H_2O = H_3PO_4.$$

This transformation is effected also by simply allowing the solution of the meta-acid in water to stand for a time, and by boiling the solution.

When a metaphosphate, as, for example, sodium metaphosphate, $NaPO_3$, is heated in contact with a metallic oxide, it takes up the oxide as the free acid takes up water, and phosphates are thus formed in which two or more metals take the place of the hydrogen of the acid. With a metallic oxide of the formula $M_2O$ it combines to form a phosphate, $M_2NaPO_4$, thus:

$$NaPO_3 + M_2O = M_2NaPO_4$$

—a kind of action which is plainly analogous to the conversion of metaphosphoric into orthophosphoric acid. So, also, when an oxide of the formula $MO$ is heated with sodium metaphosphate a phosphate of the formula $MNaPO_4$, in which M represents a bivalent metal, is formed:

$$NaPO_3 + MO = MNaPO_4.$$

Upon facts of this kind depends the power of sodium metaphosphate to *dissolve* metallic oxides, as when beads formed by heating sodium ammonium phosphate are used in analysis. The first effect of heating the phosphate is, as explained above, the formation of sodium metaphosphate which melts, forming a clear liquid known as the " bead of microcosmic salt."

**Phosphorous Acid, $H_3PO_3$.**—This acid is formed when phosphorus trichloride is treated with water. It is also formed together with phosphoric and hypophosphoric acids when phosphorus is allowed to lie in contact with moist air. The acid can be obtained from its solutions by evaporation, when it is deposited in transparent crystals. When heated it is converted into phosphoric acid, phosphine being given off:

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

This reaction has been discussed under Phosphine (which see). The tendency of phosphorous acid to take up oxygen and form phosphoric acid makes it a good reducing agent. Its action is well illustrated in the case of mercuric chloride, $HgCl_2$, which it transforms into mercurous chloride, $HgCl$. Water being present, the phosphorous acid appropriates the oxygen of a part of it, leaving the hydrogen to act upon the mercuric chloride :

$$2HgCl_2 + H_3PO_3 + H_2O = H_3PO_4 + 2HgCl + 2HCl.$$

Phosphorous acid is only dibasic, its salts having the general formula $HM_2PO_3$. This fact has led to the belief that in the acid two of the hydrogen atoms are in combination with oxygen in the form of hydroxyl, while the third is in combination with phosphorus as represented in the formula $OP\begin{cases} H \\ OH \\ OH \end{cases}$. This conclusion finds further support in the conduct of some derivatives of phosphorous acid.

**Hypophosphoric Acid, $H_4P_2O_6$,** is formed together with phosphoric and phosphorous acids when sticks of ordinary phosphorus placed in glass tubes drawn out to a small opening at one end are exposed to the action of moist air. By arranging a number of such tubes on a funnel the lower end of which is in a bottle, a solution is gradually collected which contains hypophosphoric acid together with the other two acids mentioned. The salts of the acid show that it is tetrabasic. It has been suggested that this acid has the constitution represented by the formula $\begin{array}{c} OP(OH)_2 \\ | \\ OP(OH)_2 \end{array}$.

**Hypophosphorous Acid, $H_3PO_2$,** has already been referred to, as its potassium salt is formed in the preparation of phosphine by the action of phosphorus upon a solution of potassium hydroxide :

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

The acid is a solid which crystallizes well. The most characteristic fact in its conduct is its marked tendency

to pass over into phosphoric acid by taking up oxygen. It is therefore a good reducing agent. It reduces sulphuric acid to sulphurous acid and even to sulphur, as represented in the two equations below :

$$2H_2SO_4 + H_3PO_2 = 2H_2SO_3 + H_3PO_4;$$
$$H_2SO_3 + H_3PO_2 = S + H_2O + H_3PO_4.$$

When heated, also, it forms phosphoric acid and phosphine just as phosphorous acid does :

$$2H_3PO_2 = H_3PO_4 + PH_3.$$

The acid is monobasic, and this has led to the belief that only one of the hydrogen atoms in the molecule of the acid is in combination with oxygen as hydroxyl, and that the two others are in combination with phosphorus as represented in the formula $OP\begin{cases} H \\ H \\ OH \end{cases}$. The relation between this acid and phosphorous and phosphoric acids has already been commented upon (see page 323).

**Phosphorus Pentoxide, Phosphoric Anhydride, $P_2O_5$.—** This highest oxidation-product of phosphorus is formed by burning the element in air or in oxygen. It is a white powder which attracts moisture from the air and becomes liquid. This power to combine with water is its most characteristic property. It forms first, as we have seen, metaphosphoric acid and, by further action, orthophosphoric acid. Its action towards water is strongly suggestive of the action of sulphur trioxide or sulphuric anhydride towards water. Owing to this power to combine with water, phosphorus pentoxide is used for the purpose of drying gases, and as a dehydrating agent.

**Phosphorus Trioxide, or Phosphorous Anhydride, $P_2O_3$** (or $P_4O_6$), is formed by burning phosphorus so that the air does not have free access to it, as by putting a piece of phosphorus in a glass tube drawn out to a fine opening, drawing air over the phosphorus, and warming it gently. In this way not enough air can get access to the

phosphorus to convert it into the pentoxide. The tri-oxide has such a strong tendency to pass over into the pentoxide that when brought into the air it takes fire and burns, forming the higher oxide. It is readily converted into phosphorous acid by water.

**Phosphorus Suboxide, $P_4O$,** is one of the products formed by the burning of phosphorus in a limited supply of air. It is also formed in several other ways, and two varieties of it have been described.

**Phosphorus Tetroxide, $P_2O_4$,** is also formed when phosphorus is burned in the air. It can be obtained pure in the form of colorless crystals.

**Constitution of the Acids of Phosphorus.**—Considerable has already been said on this subject in dealing with the relations between the acids. The view that phosphoric acid contains three hydroxyl groups is based upon the fact that the acid is tribasic, which, taken together with what is known in regard to the conduct of other acids, suggests that all three hydrogen atoms in the molecule are in combination with oxygen. This view is the simplest, and all facts known in regard to the conduct of phosphoric acid are in accordance with it. The constitution is represented by the formula $O=P{<}^{O-H}_{O-H}{}^{O-H}$, which may also be written in this way: $OP(OH)_3$. Two views suggest themselves in considering the constitution of phosphorous acid. It may be, like phosphoric acid, a trihydroxyl derivative of the formula $P(OH)_3$, or it may have the structure represented by the formula $O=P{<}^{H}_{OH}{}^{OH}$ or $OP\left\{{{H}\atop{(OH)_2}}\right.$. The easy formation of the acid from phosphorus trichloride and water is in accordance with the former view. On the other hand, as has already been remarked, the fact that the acid is dibasic speaks against this view, and in favor of the latter. A somewhat complex reaction of an organic derivative of phosphorous acid also furnishes evidence in favor of the view that there are only two hydroxyl groups contained in the molecule of

phosphorous acid, and that its structure is represented by the formula $O=P{\Large\langle}{\begin{smallmatrix}H\\O{-}H\\O{-}H\end{smallmatrix}}$ .

**Phosphorus Oxychloride, POCl$_3$.**—This compound has been referred to in connection with the chlorides of phosphorus. It is formed by the action of ozone on phosphorus trichloride and by the action of water upon the pentachloride :

$$PCl_3 + O \ \ = POCl_3 ;$$
$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

It may be regarded as phosphoric acid in which all three of the hydroxyl groups are replaced by chlorine, just as sulphuryl chloride, $SO_2Cl_2$, is to be regarded as sulphuric acid in which both hydroxyls are replaced by chlorine. The fact that when treated with water and other compounds containing hydroxyl it yields phosphoric acid has been mentioned, and the value of this reaction and the similar reaction of phosphorus pentachloride as a means of detecting the hydroxyl condition in compounds has been pointed out (see p. 316).

**Arsenic Acid, H$_3$AsO$_4$.**—The compound of arsenic and oxygen which is most readily obtained is the trioxide, $As_2O_3$, and this is formed by direct combination of the two elements. When this is oxidized either with *aqua regia* or by passing chlorine into water in which the trioxide is suspended it is converted into arsenic acid :

$$As_2O_3 + 3H_2O + 2O = 2H_3AsO_4.$$

From its solutions it is obtained in crystallized form. According to the temperature to which it is heated the deposit has the composition of the ortho-acid, $H_3AsO_4$, of the pyro-acid, $H_4As_2O_7$, or of the meta-acid, $HAsO_3$. Perfect analogy with the phosphorus compounds is here observed. When the pyro- and meta-acids are dissolved in water they pass at once into the form of the ortho-acid. Arsenic acid, like phosphoric acid, is a strong tribasic acid, forming three series of salts which under

the influence of heat conduct themselves like the corresponding phosphates, the primary salts yielding pyro-arsenates, and the secondary salts yielding meta-arsenates. When these are dissolved in water they pass at once into the corresponding salts of ortho-arsenic acid. Arsenic acid is easily reduced to the form of arsenic. When hydrogen sulphide is passed through a hydrochloric acid solution of arsenic acid different reactions take place according to the conditions. The three possibilities are: (1) The formation of the pentasulphide; (2) the formation of sulphoxyarsenic acid, $H_3AsO_3S$; and (3) the formation of arsenic pentasulphide, arsenic trisulphide, and sulphur. These reactions are represented by the following equations:

$$
\begin{aligned}
&(1) \quad H_3AsO_4 \quad + H_2S \ = H_3AsO_3S + H_2O\,; \\
&(2) \quad 2H_3AsO_3S + 3H_2S = As_2S_5 \quad\ + 6H_2O\,; \\
&(3) \begin{cases} 2H_3AsO_3S + 6HCl = 2AsCl_3 \quad + 6H_2O + 2S\,; \\ 2AsCl_3 \quad\ + 3H_2S = As_2S_3 \quad\ + 6HCl. \end{cases}
\end{aligned}
$$

The first action is that represented by equation (1). The acid thus formed, known as sulphoxyarsenic acid, differs from arsenic acid only in the fact that it contains a sulphur atom in the place of one oxygen atom. It is soluble in water, and, therefore, when hydrogen sulphide is passed into a solution of arsenic acid there is at first no precipitate formed; but gradually, where the hydrogen sulphide is in excess, some of the sulphoxyarsenic acid is changed to arsenic pentasulphide, while another part of the acid is decomposed by hydrochloric acid, forming arsenic chloride and sulphur, and the trisulphide is then precipitated. Therefore, the precipitate formed by passing hydrogen sulphide into a solution of arsenic acid is likely to consist of a mixture of arsenic pentasulphide, trisulphide, and sulphur.

**Arsenious Acid,** $H_3AsO_3$, is not known in the free state, but salts related to it are formed by treating arsenic trioxide with bases. Thus, when it is treated with potassium hydroxide the salt $KAsO_2$, or potassium meta-arsenite, is formed:

$$As_2O_3 + 2KOH = 2KAsO_2 + H_2O.$$

Salts of meta-arsenious acid, $AsO.OH$, are more commonly obtained than those of the normal acid, $As(OH)_3$. In alkaline solution arsenious acid tends to pass into the form of arsenic acid, and it is therefore a useful reducing agent. Its action in this way is, however, not as strong as that of phosphorous acid.

**Arsenic Trioxide, $As_2O_3$.**—This compound is commonly called arsenic or white arsenic. , It is the most important of all the compounds of the element arsenic. It finds applications for many purposes, and is manufactured in large quantities. It occurs in small quantity in nature, but that which comes into the market is manufactured by roasting natural arsenides, particularly arsenical pyrites, $FeAsS$. The products of roasting this compound are ferric oxide, $Fe_2O_3$, sulphur dioxide, $SO_2$, and arsenic trioxide, $As_2O_3$. Of these, the first is a non-volatile solid, the second a gas, and the third a volatile solid. By passing the volatile products through properly constructed canals the arsenic trioxide is condensed on the walls. Some of the powder thus obtained must be subjected to a second process of distillation to make it pure enough for the market. In a recent year over 6000 tons of this substance were produced in England and Saxony.

Arsenic trioxide is a colorless, amorphous, vitreous mass. Gradually it becomes opaque and crystalline, with an appearance like that of porcelain. It crystallizes in two forms, the common one being that of regular octahedrons. Under exceptional conditions it crystallizes in the form of rhombic prisms. When heated it sublimes, and is deposited on a cold surface in the form of octahedrons. Arsenic trioxide is difficultly soluble in water, but more easily in hydrochloric acid. The solution in hydrochloric acid contains arsenic trichloride (see p. 317), and when the solution is boiled the chloride is carried over. When the solution of the amorphous oxide in hydrochloric acid is concentrated enough it deposits the oxide in crystalline form, and the formation of the crystals is accompanied by an evolution of light which can be seen in a dark room. When the crystalline variety is dissolved it is deposited in crystals without

evolution of light. The formation of arsenic trichloride by the action of hydrochloric acid on the oxide is perfectly analogous to the formation of the chloride of any base-forming element by the action of hydrochloric acid upon the oxide, as, for example, ferric oxide. The reactions are represented thus :

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O ;$$
$$\text{and } Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

While in this reaction arsenic appears as a base-forming element, its character as an acid-forming element shows itself when the chloride is treated with a large excess of water, under which circumstances it is completely converted into the oxide. Towards some acids also arsenic trioxide acts as a weak base. A somewhat complex sulphate is known in which the arsenic replaces a part of the hydrogen of the acid. It is formed by treating the trioxide with fuming sulphuric acid.

The trioxide is easily reduced. When heated with potassium cyanide, KCN, or with charcoal in a dry glass tube arsenic is deposited above the flame in the form of a dark lustrous layer. When brought into a vessel from which hydrogen is being evolved it is reduced to arsine.

The specific gravity of the vapor of the oxide shows that it has the formula $As_4O_6$, and not $As_2O_3$; as, however, most of its reactions can be more conveniently expressed by the aid of the simpler formula, the latter is commonly used.

Arsenic trioxide has a weak, disagreeable, sweet taste, and is an active poison. A dose of from two to three grains is sufficient to cause death unless it is ejected by vomiting, or rendered harmless by being converted into an insoluble compound. It is possible, by beginning with small doses, and gradually increasing them, to accustom the human body to considerably larger doses than that mentioned. It strengthens the power of the respiratory organs, and consequently facilitates mountain-climbing. The peasants in some mountain regions are said to use it habitually. It is much used in medicine, especially in skin diseases. It is also used extensively

as a rat-poison.   The most efficient antidote is a mixture of ferric hydroxide, $Fe(OH)_3$, and magnesia, which forms with arsenic trioxide an insoluble compound.

**Arsenic Pentoxide, $As_2O_5$,** is formed by igniting arsenic acid.   If heated too high the pentoxide breaks down into arsenic trioxide and oxygen.   A marked difference will be observed between the conduct of the oxides of phosphorus and that of the corresponding oxides of arsenic.   While phosphorus trioxide takes up oxygen spontaneously when exposed to the air, and the pentoxide is not decomposed by heat, the trioxide of arsenic does not under any circumstances take up oxygen directly, and the pentoxide easily breaks down into the trioxide and oxygen when heated.

**Sulphides.**—There are three compounds of arsenic with sulphur—the disulphide, $As_2S_2$, the trisulphide, $As_2S_3$, and the pentasulphide, $As_2S_5$.

**Arsenic Disulphide, $As_2S_2$,** occurs in nature and is known as *realgar*.   It can also be obtained by melting arsenic and sulphur together in the right proportions. It forms an orange-red powder which was formerly used as a pigment.

**Arsenic Trisulphide, $As_2S_3$,** is found in nature and is called *orpiment* or king's yellow.   It can be prepared by melting together arsenic and sulphur in the proper proportions, and by precipitating a solution of arsenic trioxide in hydrochloric acid with hydrogen sulphide.   It melts, forming a red liquid.   The natural substance, as well as that which is precipitated by means of hydrogen sulphide, is yellow.   It dissolves in soluble sulphides, forming salts of sulpharsenious acid, $H_3AsS_3$, or $HAsS_2$. The salts are, for the most part, derived from the acid of the latter formula.   There is, therefore, perfect analogy between the oxygen and sulphur compounds, for, as we have seen, when arsenic trioxide is dissolved in potassium hydroxide a salt of the formula $KAsO_2$ is formed.   The analogy is clearly shown by means of the equations

$$As_2O_3 + 2KOH = 2KAsO_2 + H_2O\,;$$
$$As_2S_3 + 2KSH = 2KAsS_2 + H_2S.$$

The acid $HAsS_2$ is derived from the corresponding normal acid $As\begin{cases} SH \\ SH \\ SH \end{cases}$, by loss of one molecule of hydrogen sulphide:

$$As\begin{cases} SH \\ SH \\ SH \end{cases} = As\begin{cases} S \\ SH \end{cases} + H_2S\,;$$

just as the acid $HAsO_2$ is derived from the normal oxygen acid $As\begin{cases} OH \\ OH \\ OH \end{cases}$, by loss of one molecule of water:

$$As\begin{cases} OH \\ OH \\ OH \end{cases} = As\begin{cases} O \\ OH \end{cases} + H_2O.$$

When a solution of a sulpharsenite is treated with one of the stronger acids, as, for example, hydrochloric acid, arsenic trisulphide is precipitated. We should naturally look for the separation of the free acid according to the equation

$$KAsS_2 + HCl = HAsS_2 + KCl\,;$$

but, if this is formed, it breaks down at once into hydrogen sulphide and arsenic trisulphide:

$$2HAsS_2 = As_2S_3 + H_2S.$$

There is a striking analogy between this action and that which takes place when a stronger acid is added to a solution of a carbonate, when carbon dioxide is set free:

$$K_2CO_3 + 2HCl = H_2CO_3 + 2KCl\,;$$
$$H_2CO_3 = CO_2 + H_2O.$$

A marked difference between the two cases is to be found in the fact that the trisulphide of arsenic is insoluble in water and therefore appears as a precipitate, while carbon dioxide escapes as a gas.

Besides salts of the acids $H_3AsS_3$ and $HAsS_2$, there are others derived from the more complex acid $H_4As_2S_5$.

This bears to normal sulpharsenious acid, As(SH)$_3$, a relation similar to that which pyrophosphoric acid bears to orthophosphoric. If two molecules of the normal acid lose one molecule of hydrogen sulphide, this pyrosulpharsenious acid is the product:

$$2As\begin{cases} SH \\ SH \\ SH \end{cases} = As_2S(SH)_4 + H_2S.$$

It is a salt of this acid which is formed when arsenic trisulphide is dissolved in ammonium sulphide:

$$As_2S_3 + 2(NH_4)_2S = As_2S(SNH_4)_4.$$

**Arsenic Pentasulphide, As$_2$S$_5$,** is formed by melting sulphur and arsenic together in the proper proportions, and by precipitating a solution of sodium sulpharsenate with hydrochloric acid:

$$2Na_3AsS_4 + 6HCl = 6NaCl + As_2S_5 + 3H_2S.$$

Sulpharsenic acids corresponding to the oxygen acids suggest themselves. We might, for example, expect to find salts derived from the acids H$_3$AsS$_4$, HAsS$_3$, and H$_4$As$_2$S$_7$, corresponding to ortho-, meta-, and pyro-arsenic acids. When arsenic pentasulphide is dissolved in solutions of metallic sulphides the products are generally salts of pyrosulpharsenic acid, H$_4$As$_2$S$_7$, and these undergo decomposition into salts of the ortho- and meta-acids. When, for example, arsenic pentasulphide is dissolved in ammonium sulphide reaction takes place thus:

$$As_2S_5 + 2(NH_4)_2S = (NH_4)_4As_2S_7.$$

The ammonium salt formed in this way is, however, decomposed thus:

$$(NH_4)_4As_2S_7 = (NH_4)_3AsS_4 + (NH_4)AsS_3.$$

Only one compound intermediate between arsenic and sulpharsenic acids is known. This is the sulphoxyarsenic acid formed as the first product of the action of hydro-

gen sulphide upon a solution of arsenic acid, which was referred to under Arsenic Acid (p. 337). The possibility of other products of the formulas $H_3AsO_2S_2$ and $H_3AsOS_3$ will occur to every one.

**Antimonic Acid, $H_3SbO_4$.**—This acid is the final product of the oxidation of antimony when treated with *aqua regia.* It need only be said that it is very similar to phosphoric and arsenic acids; and that, like these, it yields a meta- and a pyro-acid of the formulas $HSbO_3$ and $H_4Sb_2O_7$. The acid of the formula $OSb(OH)_3$, or orthoantimonic acid, is known in the free state, and is formed by treating a soluble salt of antimonic acid with sulphuric or nitric acid:

$$OSb(OK)_3 + 3HNO_3 = 3KNO_3 + OSb(OH)_3.$$

An acid $Sb_2O(OH)_8$ is also known in the free state, being formed by the action of antimony pentachloride upon water. The lower oxides of antimony, the trioxide, $Sb_2O_3$, and the tetroxide, $Sb_2O_4$, are not strongly acidic; that is to say, they do not readily form salts when treated with bases. In this respect the trioxide of antimony differs markedly from the corresponding oxides of phosphorus and arsenic.

**Antimony Trioxide, $Sb_2O_3$.**—This compound is found in nature as white ore of antimony, and is easily formed by burning antimony in the air and by oxidizing it with nitric acid or saltpeter. That formed by burning antimony in the air always contains some of the tetroxide, and by heating it long enough in the air and to a temperature high enough it is completely transformed into the tetroxide. When the trioxide is dissolved in caustic soda a salt of the formula $NaSbO_2$ is formed. This is plainly derived from an acid of the formula $HSbO_2$, which bears a simple relation to normal antimonious acid. Towards most bases, however, antimony trioxide does not conduct itself as an acid. On the other hand, towards the stronger acids it acts as a base.

**Salts of Antimony.**—The salts of antimony are derived either from the hydroxide $Sb(OH)_3$, or from the hydroxide $SbO.OH$. The salts of the first class are called *anti-*

*mony salts;* those of the second class are called *antimonyl salts.* In the salts formed when the trihydroxide of antimony is completely neutralized by acids, the antimony takes the place of three atoms of hydrogen. Thus, the nitrate has the formula $Sb(NO_3)_3$; the sulphate has the formula $Sb_2(SO_4)_3$; etc. Besides these normal salts there are, however, basic salts. Thus there are two basic nitrates possible of the formulas $Sb\begin{cases} OH \\ OH \\ NO_3 \end{cases}$ and $Sb\begin{cases} OH \\ NO_3 \\ NO_3 \end{cases}$.

The formation of antimonyl salts may be illustrated by the sulphate. This may be regarded as formed by the action of sulphuric acid upon the hydroxide SbO.OH, which is analogous in composition to the acid of arsenic of the formula AsO.OH:

$$2SbO.OH + \frac{HO}{HO}\!>\!SO_2 = \frac{SbO.O}{SbO.O}\!>\!SO_2 + 2H_2O.$$

The product is *antimonyl sulphate.* The weak basic character of the hydroxides of antimony is shown by the fact that many of its salts are decomposed by water. The salt of antimony which is most commonly met with is the so-called *tartar emetic,* which appears to be an antimonyl potassium salt of tartaric acid. Tartaric acid is a dibasic acid of the formula $C_4H_4O_4\begin{cases} OH \\ OH \end{cases}$. When one of its acid hydrogen atoms is replaced by potassium, and the other by the antimonyl group SbO, the salt thus formed is tartar emetic, $C_4H_4O_4\begin{cases} OSbO \\ OK \end{cases}$. It is also possible that this salt may be derived from the trihydroxide $Sb(OH)_3$ by replacement of one hydrogen atom by potassium, and neutralization of the rest of the compound by the dibasic tartaric acid. It seems more probable, however, that when tartaric acid acts upon the compound $Sb\begin{cases} (OH)_2 \\ OK \end{cases}$ it first appropriates the potassium atom, forming acid potassium tartrate, and that the antimony trioxide being basic is neutralized by the acid tartrate. To decide between the two views is at present impossible.

Antimony trioxide dissolves in hydrochloric acid, forming the trichloride, and this, as has been stated, is decomposed by water yielding oxychlorides.

**Antimony Tetroxide, $Sb_2O_4$.**—This compound is most easily obtained by igniting antimonic acid, $H_3SbO_4$. Two reactions are of course involved :

$$2H_3SbO_4 = Sb_2O_5 + 3H_2O ;$$
$$Sb_2O_5 \quad = Sb_2O_4 + O.$$

It is also formed by igniting the trioxide in the air. At ordinary temperatures the tetroxide is white, but it becomes yellow when heated. Towards strong acids this oxide acts like a weak base. A potassium salt of the formula $K_2Sb_2O_5$ is known, which is derived from the acid $H_2Sb_2O_5$, and this in turn from the simpler acid $SbO(OH)_2$ by loss of water. The oxide itself is regarded by some as an antimonyl salt of metantimonic acid, $SbO_2.OH$, of the formula $SbO_2.O.SbO$.

**Antimony Pentoxide, $Sb_2O_5$.**—The tetroxide of antimony does not combine with oxygen to form the pentoxide. The latter can be obtained only by gentle ignition of antimonic acid, care being taken not to raise the temperature high enough to decompose the pentoxide into the tetroxide and oxygen. The fact that the pentoxide readily yields salts of antimonic acid when treated with basic solutions was mentioned under Antimonic Acid.

**Antimony Trisulphide, $Sb_2S_3$.**—This compound occurs in nature in considerable quantity and is the chief source of antimony. It is known as *stibnite* and *antimony blende*. In some localities, especially in Japan, it occurs in large crystals of great beauty. When heated in the air, or roasted, it is converted into the trioxide, and finally into the tetroxide, while the sulphur escapes as the dioxide. Hydrochloric acid dissolves the trisulphide in the form of the chloride with evolution of hydrogen sulphide :

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Nitric acid converts it into the oxide with separation of sulphur. When a solution of antimony chloride is treated with hydrogen sulphide, the trisulphide is thrown

down. This artificially prepared trisulphide has an orange-red color, while that which occurs in nature is black or gray. The sulphide dissolves in solutions of metallic sulphides, forming salts of sulphantimonious acid, either $SbS.SH$ or $Sb(SH)_3$.

**Antimony Pentasulphide, $Sb_2S_5$,** is formed by passing hydrogen sulphide into a solution of antimonic acid or by decomposing a salt of sulphantimonic acid by means of an acid. The action takes place thus:

$$2H_3SbO_4 + 5H_2S = Sb_2S_5 + 8H_2O \;;$$
$$2Na_3SbS_4 + 6HCl = 6NaCl + Sb_2S_5 + 3H_2S.$$

It is, when dry, a golden-yellow powder known as *sulphur auratum*. It dissolves easily in solutions of metallic sulphides, forming the *sulphantimonates*, of which the sodium salt, $Na_3SbS_4$, known as Schlippe's salt, is a good example. The action is represented by this equation:

$$Sb_2S_5 + 6NaSH = 2Na_3SbS_4 + 3H_2S.$$

When heated in the air the pentasulphide gives off enough sulphur to form the trisulphide; while when the pentoxide is heated it is converted into the tetroxide. The sulphantimonates are decomposed when treated with acids and the pentasulphide is thrown down.

**Constitution of the Acids of Arsenic and Antimony.—** There is, in general, marked analogy between the compounds of phosphorus and those of arsenic and antimony. In one particular, however, there is a difference which is worthy of special mention. It appears that, while phosphorous acid is dibasic and probably has the structure $OP\begin{cases} H \\ OH \\ OH \end{cases}$, arsenious and antimonious acids are the normal compounds represented by the formulas $As(OH)_3$ and $Sb(OH)_3$. Arsenic and antimonic acids appear to have the same structure as phosphoric acid represented by the formulas $As\begin{cases} O \\ (OH)_3 \end{cases}$ and $Sb\begin{cases} O \\ (OH)_3 \end{cases}$. The difference between phosphorous and arsenious acids suggests the difference between sulphurous and selenious

acids. While, according to the evidence, the constitution of sulphurous acid is that represented by the formula $O_2S \begin{cases} H \\ OH \end{cases}$, that of selenious acid is represented by the formula $OSe \begin{cases} OH \\ OH \end{cases}$.

**Oxychlorides of Antimony.**—Under the head of Antimony Trichloride the fact was mentioned that this compound is decomposed by cold water as represented in the equation

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

If, however, hot water is used, the composition of the product approximates to that represented by the formula $Sb_4O_5Cl_2$. This complex mixture of oxychlorides is known as the "*Powder of Algaroth.*" It may be regarded as derived from the simple oxychloride by loss of antimony trichloride, thus:

$$5SbOCl = Sb_4O_5Cl_2 + SbCl_3.$$

Many other oxychlorides besides the two mentioned have been obtained, but they are all more or less closely related to the simple compound SbOCl.

**Oxides of Bismuth.**—The principal compound of bismuth and oxygen is the trioxide, $Bi_2O_3$, which is formed when bismuth is burned in the air. It is a yellow powder. Besides the method just mentioned, it is formed by decomposing bismuth nitrate by high heat. If a solution of bismuth nitrate, $Bi(NO_3)_3$, is treated with a cold solution of potassium hydroxide, bismuth hydroxide, $Bi(OH)_3$, is thrown down. When this is dried at 100° it loses water and is converted into the hydroxide, $BiO(OH)$; and if the hydroxide first precipitated is boiled with the solution it is converted into the yellow oxide, $Bi_2O_3$. The reactions involved are

$$Bi(NO_3)_3 + 3KOH = Bi(OH)_3 + 3KNO_3;$$
$$Bi(OH)_3 = BiO.OH + H_2O;$$
$$2Bi(OH)_3 = Bi_2O_3 + 3H_2O.$$

The trioxide of bismuth is basic and forms salts which in composition correspond to the salts of antimony.

Like the latter, they are of two classes—the *bismuth salts* and the *bismuthyl salts*. The former are derived from the triacid base, $Bi(OH)_3$, the latter from the monacid base, $BiO(OH)$.

**Salts of Bismuth.**—The best known salts of bismuth are those which it forms with sulphuric and with nitric acids. There is a sulphate of the formula $BiH(SO_4)_2$, formed by dissolving bismuth oxide in dilute sulphuric acid. The sulphate which is most stable in the presence of water is the bismuthyl salt, $(BiO)_2SO_4$. When bismuth is dissolved in nitric acid and the solution evaporated to dryness the salt $Bi(NO_3)_3 + 10H_2O$ is obtained. This salt is decomposed when heated, and by water, forming *basic nitrates of bismuth.* The composition of the basic nitrate obtained by decomposing the neutral nitrate with water differs according to the conditions. Hot and cold water produce different results. A solution containing much nitric acid does not give the same result as one which contains little, etc. As basic bismuth nitrate is used in medicine it is necessary that specific directions should be given for its preparation, in order that a substance of the same composition should always be obtained. Among the basic nitrates which have been isolated are the following: $Bi \begin{cases} (OH)_2 \\ NO_3 \end{cases}$, $BiO.NO_3$ and $Bi \begin{cases} O.BiO \\ O.NO_2 \\ OH \end{cases}$. Besides these many of much more complex composition are known, but all of them can be referred to the simple forms. Some of them are of special interest, as they appear to be derived from complex forms of nitric acid, as, for example, an acid of the formula $N_2O_3(OH)_4$ or $H_4N_2O_7$, which is analogous to pyrophosphoric, pyroarsenic, and pyroantimonic acids. The basic nitrate of bismuth, or the *subnitrate*, as it is frequently called in pharmacy, is much used in medicine as a remedy in dysentery and cholera. It is also used as a cosmetic.

**Bismuth Dioxide, $Bi_2O_2$,** is formed as a brown precipitate when potassium hydroxide is added to a solution of

bismuth chloride and stannous chloride, $SnCl_2$. Stannous chloride combines very readily with chlorine to form stannic chloride, $SnCl_4$. When, therefore, stannous chloride and bismuth chloride are brought together, it is probable that the former extracts a part of the chlorine from the latter, forming a chloride of the formula $BiCl_2$, and this with the potassium hydroxide breaks down, yielding the dioxide :

$$2BiCl_3 + SnCl_2 = 2BiCl_2 + SnCl_4 ;$$
$$2BiCl_2 + 4KOH = Bi_2O_2 + 4KCl + 2H_2O.$$

**Bismuth Pentoxide, $Bi_2O_5$,** is formed by oxidizing the trioxide, by means of chlorine, in alkaline solution. Although some experimenters appear to have obtained salts of bismuthic acid, as, for example, $KBiO_3$, others have failed to obtain them. In any case it is evident that the acid properties of the oxide are very weak.

**Bismuth Trisulphide, $Bi_2S_3$,** occurs in nature, and is formed by precipitating bismuth from solutions of its salts with hydrogen sulphide. It dissolves in hot concentrated hydrochloric acid and in nitric acid. It does not dissolve in solutions of the sulphides as the sulphides of arsenic and antimony do.

**Bismuth Oxychloride, BiOCl,** which in composition is analogous to the simplest form of antimony oxychloride, is thrown down as a white powder when a solution containing bismuth chloride is treated with water :

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

### FAMILY V, GROUP A.

As the members of Group A, Family VII, are related to Group B of the same family ; and as the members of Group A, Family VI, are related to the members of Group B of the same family, so the members of Group A, Family V, are related to the members of Group B, which have just been studied. The members of Group A are vanadium, columbium, tantalum, and didymium, all of which are rare. Of these vanadium has been most thoroughly investigated, and columbium next.

**Vanadium, V (At. Wt. 50.99).** —This element occurs in nature in the form of vanadates or salts of vanadic acid, $H_3VO_4$, which is analogous to phosphoric acid. The methods employed in separating the element from its compounds depend upon the composition of the compound. In the separation advantage is frequently taken of the fact that the ammonium salt of vanadic acid is difficultly soluble in a solution of ammonium chloride. When this ammonium salt is ignited it is converted into the pentoxide $V_2O_5$. With chlorine, vanadium forms the compounds $VCl_2$, $VCl_3$, and $VCl_4$; with oxygen, the compounds $V_2O$, $V_2O_2$, $V_2O_3$, $V_2O_4$, and $V_2O_5$. In its relations to oxygen it suggests nitrogen. The oxide, $V_2O_4$, conducts itself something like the tetroxide of antimony. Towards strong bases it acts like an acid, forming salts of the general formula $V_4O_7(OM)_2$. (See Antimony Tetroxide.)

**Vanadic Acid, $H_3VO_4$,** is the most important and best known of the compounds of vanadium. It is the final product of the oxidation of vanadium, and bears to this element the same relation that phosphoric, arsenic, and antimonic acids bear to phosphorus, arsenic, and antimony. The vanadates are derived from ortho-, meta-, and pyro-vanadic acids, though the most stable ones are the metavanadates, $MVO_3$. The free *metavanadic acid* is known. It is a beautiful golden-yellow compound, which may be used as a substitute for gold bronze. An oxychloride of the formula $VOCl_3$, corresponding to phosphorus oxychloride, is made by direct addition of chlorine to vanadium dioxide.

**Tantalum, Ta (At. Wt. 181.45).** —Tantalum occurs in the minerals columbite and tantalite, accompanied by niobium. With the members of the chlorine group it forms the compounds $TaF_5$, $TaCl_5$, $TaBr_5$, and $TaI_5$. Tantalum fluoride combines easily with the fluorides of other metals forming the fluotantalates. These may be regarded as salts of fluotantalic acid, which are derived from the oxygen acids by replacement of a part or all of the oxygen by fluorine. Thus, the salt $K_2TaF_7$ is easily obtained by treating tantalum fluoride with a solution of potassium

fluoride. This is a salt of the acid $H_2TaF_7$ or $H_4Ta_2F_{14}$, which is analogous to the oxygen acid $H_4Ta_2O_7$. With oxygen it forms $Ta_2O_4$ and $Ta_2O_5$. The latter forms the tantalates with bases. When tantalum pentachloride is decomposed with water it forms the acid $H_4Ta_2O_7$ or pyrotantalic acid :

$$2TaCl_5 + 7H_2O = Ta_2O_3(OH)_4 + 10HCl.$$

The tantalates are derived from the meta-acid $HTaO_3$, and from the hexa-acid $H_8Ta_6O_{19}$, which is derived from the ortho-acid as represented in this equation :

$$6H_3TaO_4 = H_8Ta_6O_{19} + 5H_2O.$$

**Columbium, Cb** (At. Wt. 93.7).—This element, which is sometimes called niobium, occurs in the mineral columbite. It forms two chlorides, $CbCl_3$ and $CbCl_5$, and a bromide and fluoride corresponding to the latter chloride. The fluoride readily forms *fluocolumbates*, similar to the fluotantalates. The niobates are derived from a number of forms of the acid which are, however, closely related to the ortho-acid $H_3CbO_4$.

**Didymium** consists of two very similar elements, *neodymium* and *praseodymium*. In some of their compounds they show a resemblance to the members of this group. They form, for example, an oxide of the formula $Di_2O_5$. On the other hand, they seem to be more closely related to cerium and lanthanum, which are also very rare elements, occurring associated with didymium. These will be further treated of in connection with lanthanum and cerium.

## BORON, B (At. Wt. 10.86).

**General.**—Although the element boron is not a member of the family to which nitrogen and phosphorus belong, it nevertheless resembles the members of this family in some respects. It belongs to the same family as aluminium, and in the composition of its compounds it is undoubtedly similar to aluminium ; but, on the other hand, its oxide is distinctly acidic, while that of aluminium is basic.

**Occurrence.**—Boron occurs in nature chiefly in the form of boric acid, or as salts of this acid, particularly a sodium salt known as borax.

**Preparation.**—From borax and the other borates the acid can easily be obtained. When heated, water is given off, and boron trioxide, $B_2O_3$, is left:

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$

By heating the oxide with potassium amorphous boron is obtained. By melting the oxide with aluminium, boron is formed and is dissolved in the molten aluminium, from which, on cooling, it is deposited in crystals. Amorphous boron in almost pure form is obtained by heating borax with magnesium powder. One of the chief difficulties encountered in preparing boron is to prevent the element from combining with the nitrogen of the air. At the high temperature at which the reduction takes place the two elements combine very readily to form the compound boron nitride, BN. The crystals obtained in the process described are not pure boron, but contain aluminium, or carbon and aluminium, apparently in combination with the boron. The crystals are very hard, and some of them have a high lustre.

**Properties.**—Amorphous boron is a greenish-brown powder. It burns when heated in the air or in oxygen, the product being the trioxide $B_2O_3$. Strong oxidizing agents, like nitric acid and saltpeter, readily oxidize it, forming boric acid. It combines readily also with many other elements, as with chlorine, nitrogen, and sulphur. When it is brought into the melting hydroxides or carbonates of potassium or sodium, it forms borates of the corresponding metals.

**Boron Trichloride, $BCl_3$.**—This compound is formed by heating boron in a current of dry chlorine, and by heating a mixture of boron trioxide and charcoal in chlorine:

$$2B_2O_3 + 3C + 6Cl_2 = 4BCl_3 + 3CO_2.$$

This reaction is especially interesting on account of its double character. Carbon alone could not reduce the

boron trioxide at the temperature employed ; nor could the chlorine alone displace the oxygen and form the chloride, but when both chlorine and carbon act together these changes take place, one aiding the other.

The chloride is a liquid which boils at 17°. Like phosphorus trichloride, it is easily decomposed by water, forming boric acid, which, as will be seen, is analogous in composition to phosphorous acid and arsenious acid :

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

This decomposition is analogous to that of arsenic trichloride rather than to that of phosphorus trichloride, for in the latter case a secondary change takes place, resulting in the formation of an acid of the constitution $OP \begin{cases} H \\ (OH)_2 \end{cases}$.

**Boron Trifluoride, BF₃**, is obtained by treating a mixture of fluor-spar and boron trioxide with concentrated sulphuric acid. The reaction is a double one, consisting, first, in the setting free of hydrofluoric acid from the fluor-spar :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF ;$$

and, second, in the action of the hydrofluoric acid upon the oxide of boron :

$$B_2O_3 + 6HF = 2BF_3 + 3H_2O.$$

It is a colorless gas, which acts upon water, and therefore forms a thick white cloud in the air. The action upon water is represented by the equation

$$4BF_3 + 3H_2O = B(OH)_3 + 3HBF_4.$$

The first action which we should expect is the formation of normal boric acid, thus :

$$BF_3 + 3H_2O = B(OH)_3 + 3HF.$$

But the hydrofluoric acid combines with some of the trifluoride of boron, forming the compound HBF₄, which is known as fluoboric acid. Several elements act in this

way, particularly the members of the silicon group. Silicon itself forms the well-known compound fluosilicic acid. *Fluoboric acid* is to be regarded as metaboric acid, $HBO_2$, in which the two oxygen atoms have been replaced by fluorine. The acid has been obtained in the free state, and is a liquid boiling at 120°. It forms salts of the general formula $MBF_4$, of which the potassium salt, $KBF_4$, is the best example.

**Boric Acid, $B(OH)_3$.**—Boric acid occurs free in nature and in the form of salts, of which the principal one is borax. Besides borax, which is a sodium salt derived from tetraboric acid, $H_2B_4O_7$, there are other natural borates, as boracite, which is a magnesium salt combined with magnesium chloride; and datholite, which is made up of silicic acid, boric acid, and the element calcium. One of the most interesting natural forms of boric acid is that which is given off from the earth with steam. Such jets of steam are met with in many volcanic regions, and are called fumaroles. In Tuscany many of the fumaroles are charged with small quantities of boric acid, which is somewhat volatile with steam. Those at Monte Cerboli and Monte Rotundo in Tuscany are utilized for the purpose of obtaining the boric acid. For this purpose basins are built over the fumaroles and filled with water, so that the steam is condensed and the boric acid dissolved in the water. The solutions formed at the higher levels flow into basins at lower levels, and finally become charged with a considerable quantity of the acid, when it is evaporated to crystallization by the aid of the heat furnished by the fumaroles. The acid obtained in this way is not pure, but by recrystallization it is easily purified.

Boric acid can also be made from borax by heating the salt in solution with dilute sulphuric acid :

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4B(OH)_3.$$

If the solution is sufficiently concentrated the boric acid crystallizes out on cooling.

Boric acid is easily soluble in water, and crystallizes from the solution. It is also soluble in alcohol, and this

solution burns with a characteristic green flame. The acid is quite volatile with water vapor. When heated at 100° orthoboric acid loses one molecule of water, and is converted into *metaboric acid*, $HBO_2$; at 160° it yields *tetraboric acid*, $H_2B_4O_7$; and at a higher temperature it is converted into boron trioxide or boric anhydride, $B_2O_3$. These changes are represented in the equations following:

$$B\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right. = B\left\{\begin{array}{l}O\\OH\end{array}\right. + H_2O;$$

$$\begin{array}{l}B{\nearrow}^{OH}_{-OH}{\searrow}_{OH}\\[4pt]B{\nearrow}^{OH}_{-OH}{\searrow}_{OH}\\[4pt]B{\nearrow}^{OH}_{-OH}{\searrow}_{OH}\\[4pt]B{\nearrow}^{OH}_{-OH}{\searrow}_{OH}\end{array} = \begin{array}{l}B{=}O\\{\searrow}O\\B{\nearrow}^{OH}_{O}\\B{\nearrow}^{OH}_{O}\\B{=}O\end{array} + 5H_2O.$$

The most stable salts are the tetraborates and metaborates. Borax is the sodium salt of tetraboric acid, $Na_2B_4O_7$. The salts of orthoboric acid are unstable. They break down when treated with water, forming free boric acid and either metaborates or tetraborates.

When heated together with oxides, boric oxide forms salts just as boric oxide and water form boric acid. Borax also, when treated with metallic oxides, forms double borates, which are derived from normal boric acid. Thus with copper oxide action takes place which should probably be represented thus:

$$Na_2B_4O_7 + 5CuO = Na_2Cu_5(BO_3)_4;$$

and $\quad B_2O_3 \quad + 3CuO = Cu_3(BO_3)_2.$

Many of these salts are colored, and the action of metallic compounds upon boron trioxide and upon borax is utilized for the purpose of determining their nature

by the color of the mass formed. It will be remembered that sodium metaphosphate is used in the same way. With it the oxides form salts of phosphoric acid.

Most of the boric acid obtained from Tuscany is used in the manufacture of borax, a salt which finds extensive application.

**Salts of Boron.**—Although the most characteristic compounds of boron are those in which it acts as an acid-forming element, it forms some compounds in which its power as a base-former is shown. Thus, with concentrated sulphuric acid the trioxide forms a compound which appears to be pyrosulphuric acid, $H_2S_2O_7$, in which one hydrogen is replaced by the group BO, which is analogous to antimonyl, SbO, and bismuthyl, BiO. It has the composition $(BO)HS_2O_7$. Further, when concentrated phosphoric acid acts upon crystallized boric acid, *boron phosphate*, $BPO_4$, is formed. This compound is characterized by great stability. Concentrated acids, for example, do not decompose it. It also forms a salt which appears to be analogous to tartar emetic, which, as has been pointed out, is probably antimonyl potassium tartrate, $C_4H_4O_6 \begin{cases} SbO \\ K \end{cases}$. This is the salt represented by the formula $C_4H_4O_6 \begin{cases} BO \\ K \end{cases}$, which may be called boryl potassium tartrate.

**Nitrogen Boride, BN.**—This compound has been referred to in connection with the preparation of boron. It is easily obtained by igniting a mixture of dehydrated borax and ammonium chloride. It forms a white powder, which is insoluble in water, and is characterized by great stability. At red heat it is decomposed by water vapor into ammonia and boric acid:

$$2BN + 6H_2O = 2B(OH)_3 + 2NH_3.$$

# CHAPTER XIX.

**Introductory.**—Carbon bears to Family IV relations similar to those which nitrogen, oxygen, and fluorine bear to Families V, VI, and VII. Towards hydrogen, as well as towards chlorine and oxygen, carbon is quadrivalent, and towards oxygen it is also bivalent. In this family the maximum oxygen-valence coincides with the hydrogen-valence, while, as has been seen, in Families V, VI, and VII, the oxygen-valence is higher than the hydrogen-valence, the difference becoming greater from Family V to VII. While the higher oxygen compounds of Family IV are acidic, forming acids which are derived from the normal acid, $R(OH)_4$, the lower oxides are not generally acid. The hydrogen compounds of the general formula $MH_4$, of which there are but two, those of carbon and silicon, have neither acid nor basic properties. Carbon is distinguished by the large number of the compounds into which it enters, all of which are more or less closely related to a comparatively small number of fundamental forms. Silicon also forms a large number of compounds, as we shall see ; but these are of a different kind from those obtained from carbon.

**Occurrence of Carbon.**—In general, substances which are obtained from the vegetable or animal kingdom *blacken* when heated to a sufficiently high temperature, and afterwards, if they are heated in the air, they burn up, as we say. When we consider the great variety of substances found in living things, it certainly appears remarkable that nearly all have this property in common. It is due to the fact that *nearly all animal and vegetable substances contain the element carbon.* When they are heated the

other elements present are first driven off in various forms of combination, while the carbon is the last to go. Hydrogen and oxygen pass off as water; hydrogen and nitrogen as ammonia; and much of the carbon also passes off in combination with hydrogen, with hydrogen and oxygen, and with nitrogen and hydrogen. If the heating is carried on in the air, the carbon finally combines with oxygen to form a colorless gas—it burns up. Carbon is the central element of organic nature. There is not a living thing, from the minutest microscopic animal to the mammoth, from the moss to the giant tree, which does not contain this element as an essential constituent. The number of the compounds which it forms is almost infinite, and they present such peculiarities that they are commonly treated of under a separate head, "Organic Chemistry." There is no good reason for this, except the large number of the compounds. For our present purpose it will suffice to consider the chemistry of the element itself, and of a few of its more important simple compounds.

From what has already been said, it will be seen that the principal form in which carbon occurs in nature is in combination with other elements. It occurs not only in living things, but in their fossil remains, as in coal. Coal-oil, or petroleum, the formation of which is perhaps due to the action of water on metallic carbides, consists of a large number of compounds which contain only carbon and hydrogen. Most products of plant-life contain the elements carbon, hydrogen, and oxygen. Among the more common of these products may be mentioned sugar, starch, and cellulose. Most products of animal life contain carbon, hydrogen, oxygen, and nitrogen. Among them may be mentioned albumen, fibrin, casein, etc. Carbon occurs in the air in the form of carbon dioxide. It also occurs in the form of salts of carbonic acid; the carbonates, which are very widely distributed, forming whole mountain ranges. Limestone, marble, and chalk are varieties of calcium carbonate.

Uncombined, the element occurs pure in two very dif-

ferent forms in nature: (1) As *diamond;* and (2) as *graphite*, or *plumbago.*

**Diamond.**—The diamond occurs in but few places on the earth, and practically nothing is known as to the conditions which gave rise to its formation. The celebrated diamond beds are in India, Borneo, Brazil, and South Africa. When found, diamonds are generally covered with an opaque layer, which must be removed before its beautiful properties are apparent. The crystals are sometimes regular octahedrons, though usually they are somewhat more complicated, and the faces are frequently curved. It is the hardest substance known. For use as a gem it must be cut and polished. The object in view is to bring out as strikingly as possible its brilliancy by exposing the faces favorably to the action of the light. If heated to a very high temperature without access of air, it swells up and is converted into a black mass resembling coke. The change takes place without loss in weight. Heated to a high temperature in oxygen, it burns up, yielding only carbon dioxide. It is insoluble in all known liquids at ordinary temperatures. It dissolves, however, in molten cast iron and in some other molten metals. Small diamonds have recently (1897) been made by Moissan by dissolving carbon in cast iron with the aid of an electric furnace, and suddenly cooling the mass. Under these conditions the carbon is under great pressure.

**Graphite.**—Graphite, or plumbago, is found in nature in large quantities. Sometimes it is crystallized, but in forms entirely different from those assumed by the diamond. It can be prepared artificially by dissolving charcoal in molten iron, from which solution, on cooling, it is partly deposited as graphite. It has a grayish-black color and a metallic lustre. It is quite soft, leaving a leaden-gray mark on paper when drawn across it, and it is hence used in the manufacture of so-called *lead* pencils. It is sometimes called black-lead. When heated without access of air it remains unchanged. Heated to a very high temperature in the air, or in oxygen, it burns up, forming

only carbon dioxide. Like the diamond, it is insoluble in all known liquids at ordinary temperatures.

**Amorphous Carbon.**—All forms of carbon which are not diamond, nor graphite, are included under the name *amorphous carbon.* The name signifies simply that it is not crystallized. The most common form of amorphous carbon is ordinary charcoal.

*Charcoal* is that form of carbon made by the *charring process*, which consists simply in heating wood without a sufficient supply of air to effect complete combustion. The substance almost exclusively used in the manufacture of charcoal is wood. As has already been stated, wood is made up of a large number of substances, nearly all of which, however, consist of the three elements carbon, hydrogen, and oxygen. One of the chief constituents of all kinds of wood is cellulose. Now, when we set fire to a piece of wood,—that is to say, when we heat it up to the temperature at which oxygen begins to act on it,—it burns, if air is present. Under ordinary circumstances the chemical changes which take place are complex ; but if care is taken, the combustion can be made complete, when all the carbon is converted into carbon dioxide, and all the hydrogen into water. If, on the other hand, the air is prevented from coming in contact with the wood, as by heating it in a closed vessel, or if it is prevented from coming in contact with it sufficiently to effect complete combustion, the hydrogen is given off partly as water and partly in the form of volatile products containing carbon and oxygen, as *wood spirits* or *methyl alcohol, pyroligneous* or *acetic acid, acetone*, etc. The carbon, however, is for the most part left behind as charcoal, as there is not enough oxygen to convert it into carbon dioxide. Such a process as that just described, when carried on in closed vessels, is known as *destructive distillation* or *dry distillation.* It is also known as the charring process. It is a complex example of a kind of change which we have already had to deal with. Whenever chemical compounds are heated the constituents tend to arrange themselves in forms which are stable at the higher temperature. Sulphites become sulphates ;

phosphites become phosphates; chlorates become per-chlorates; ammonium salts break down into the acids and ammonia; ammonium nitrite is decomposed into nitrogen and water; ammonium nitrate yields nitrous oxide and water; primary phosphates yield metaphosphates; secondary phosphates yield pyrophosphates, etc., etc. Carbon compounds are, in general, more sensitive to the influence of heat than the compounds of other elements, and all are decomposed even at comparatively low temperatures.

The above statements will make it possible to understand the working of a charcoal-kiln. This consists essentially of a pile of wood arranged to leave spaces between the pieces, and covered with some rough material through which the air will not pass easily, as, for example, a mixture of powdered charcoal, turf, and earth. Small openings are left in this covering, so that after the wood is kindled it will continue to burn slowly. The process is sometimes carried on in structures of brickwork with the necessary number of small openings in the walls. The changes above mentioned take place, the gases or volatile substances passing out of the top of the kiln, and appearing as a dense cloud. In due time the holes through which the air gains access to the wood, thus making the burning possible, are stopped up, and the burning ceases. Charcoal, which is impure amorphous carbon, is left behind. As wood always contains some incombustible substances in small quantity, these are, of course, found in the charcoal. When the wood or charcoal is burned, these substances remain behind as the ash.

Ordinary charcoal is a black, comparatively soft substance. It burns in the air, though not easily, unless the gases which are formed are constantly removed and fresh air is supplied,—conditions which are met by a good draught, or by blowing upon the fire with a bellows. It burns readily in oxygen. The product of the combustion in the air and in oxygen, when the conditions are favorable, is carbon dioxide, $CO_2$. In the air, when the draught is bad, another compound of carbon and oxygen,

carbon monoxide, CO, is formed.  Heated without access of air, charcoal remains unchanged.  Charcoal is insoluble in liquids generally, though it is soluble in molten iron, and it crystallizes from the solution, as we have seen, in the form of graphite, and sometimes as diamond.

*Coke.*—Besides wood charcoal, there are other forms of amorphous carbon, which are manufactured for special purposes, or are formed in processes carried on for the sake of other products.  Coke is a form of amorphous carbon which is made by heating ordinary gas-coal without access of air, as is done on the large scale in the manufacture of illuminating gas.  Coke bears to coal much the same relation that charcoal bears to wood.

*Lamp-black* is a very finely divided form of charcoal which is deposited on cold objects placed in the flames of burning oils.  The oils consist almost exclusively of carbon and hydrogen.  When burned in the air they yield carbon dioxide and water.  If the flame is cooled down by any means, or if the supply of air is partly cut off, the carbon is not completely burned, the flame "smokes," as we say, and deposits soot.  This process is chemically analogous to the deposit of metallic arsenic from a flame of arsine, to the deposit of sulphur from a flame of hydrogen sulphide, and that of phosphorus from a flame of phosphine, when these gases are burned in a supply of air insufficient to effect complete combustion of both constituents.  The soot obtained from the flames of burning oils is made up largely of fine particles of carbon, though some of the unchanged oils are contained in it.  It is used in the manufacture of printing-ink.  As carbon is acted upon directly by very few substances, and is not soluble, it is almost impossible to destroy the color of printing-ink without destroying the material upon which it is impressed.

*Bone-black,* or *Animal Charcoal,* is a form of amorphous carbon which is made by charring bones.  Bones consist of about one third organic matter and two thirds incombustible matter, mostly calcium phosphate.  When charred, the organic matter undergoes the changes briefly described under the head of Charcoal, while the

incombustible constituents remain unchanged. As the organic matter is distributed through the substance of the bones the charcoal obtained in this way is in a very fine state of division, but it is mixed with several times its own weight of mineral matter. In order to remove the latter the bone-black must be treated with hydrochloric acid, and afterwards thoroughly washed with water. An efficient variety of animal charcoal is made, further, by mixing blood with sodium carbonate, charring, and afterwards dissolving out the sodium carbonate with water.

Bone-black and wood-charcoal are very porous, and have the power to absorb gases. When placed in air containing bad-smelling gases these are absorbed, and the air is thus to some extent purified. When water containing disagreeable substances is treated with charcoal, these are wholly or partly absorbed, and the water is improved. Charcoal-filters are therefore extensively used. A charcoal-filter to be efficient should be of good size, and from time to time the charcoal should be taken out and renewed. The small filters which are screwed into faucets are of little value, as the charcoal soon becomes charged with the objectionable material which is present in the water, and is then a source of contamination rather than a means of purification. The power of charcoal to absorb gases depends upon its porosity. That from some varieties of wood is more porous than that from other varieties. Box-wood charcoal has been shown to absorb 90 times its own volume of ammonia gas, 35 times its volume of carbon dioxide, and nearly twice its volume of hydrogen. Charcoal from cocoa-nut wood absorbs 172 times its volume of ammonia, and 68 times its volume of carbon dioxide.

Some coloring matters can be removed from liquids by passing the liquids through *bone-black filters*. On the large scale, this fact is taken advantage of in the refining of sugar. The solution of sugar first obtained from the cane or beet is highly colored; and, if it were evaporated, the sugar deposited from it would be dark-colored. If, however, the solution is first passed through bone-

black filters, the color is removed, and now, on evaporating, white sugar is deposited. In the laboratory constant use is made of this method for decolorizing liquids. The action can easily be shown by adding a little bone-black to a solution containing some litmus or indigo. If the solution is digested for a short time with the bone-black, and then passed through a filter, it will be found that the coloring matter is removed.

Charcoal does not undergo decay in the air or under water nearly as readily as wood. That is another way of stating the chemical fact that the substances of which wood is made up are more susceptible to the action of other chemical substances than charcoal is. We have one good illustration of this, indeed, in the relative ease with which charcoal and wood burn in the air. Piles which are driven below the surface of water are sometimes charred to protect them from the action of those substances which cause decay.

Coal.—Under this head are included a great many kinds of impure amorphous carbon which occur in nature. Although we might distinguish between an almost infinite number of kinds of coal, for ordinary purposes they are divided into *hard* and *soft coals*, or *anthracite* and *bituminous coals*. Then there are substances more nearly allied to wood called *lignite*, and those which represent a very early stage in the process of coal-formation, viz., *peat*. A close examination or all these varieties has shown that they have been formed by the gradual decomposition of vegetable matter in an insufficient supply of air. The process has been going on for ages. Sometimes the substances have, at the same time, been subjected to great pressure, as can be seen from the position in which they occur in the earth. The products in the earlier stages of the coal-forming process are more closely allied to wood than those in the later stages. All forms of coal contain other substances in addition to the carbon. The soft coals are particularly rich in other substances. When heated they give off a mixture of gases and the vapors of volatile liquids. The gases are, for the most part, useful for illuminating

purposes. The liquids form a black, tarry mass known as *coal-tar*, from which many valuable compounds of carbon are obtained. The gases are passed through water for the purpose of removing certain impurities. This water absorbs ammonia, and forms the *ammoniacal liquor* of the gas-works, which, as has been stated, is the principal source of ammonia.

**Diamond, Graphite, and Charcoal are Different Forms of the Element Carbon.**—We have seen that oxygen presents itself in two forms—ordinary oxygen and ozone. Ozone is made from oxygen, and oxygen from ozone, without any increase or decrease in weight; and the compounds obtained by the combination of other elements with oxygen are identical with those obtained by the combination of the same elements with ozone. So also there are several varieties of sulphur, two of which crystallize in different forms. There are, further, three or four different modifications of the element phosphorus, and these differ from one another in a very marked way. The explanation of the difference between oxygen and ozone is that the molecule of the former is made up of two atoms, while that of ozone is made up of three, which are in a state of unstable equilibrium. This explanation is reached through a study of the specific gravity of the two gases. At present no satisfactory explanation can be given of the difference between the varieties of phosphorus and between the varieties of sulphur. It will probably be shown tc be due to the way in which the atoms are grouped together in the molecules, and also to the way in which the molecules are grouped together to form the masses. Carbon, as we have seen, occurs in three distinct forms. It is difficult to conceive that the black, porous charcoal, and the dull, gray, soft graphite are chemically identical with the hard, transparent, brilliant diamond. Yet this is undoubtedly the case, as can be shown by a very simple experiment. Each of the substances when burned in oxygen yields carbon dioxide. Now, the composition of carbon dioxide is known, so that, if the weight of the carbon dioxide formed in a given experiment is known, the weight of the

carbon in it is also known. When a gram of pure char-coal is burned it yields $3\frac{2}{3}$ grams carbon dioxide, and in this quantity of carbon dioxide there is contained exactly one gram of carbon. Further, when a gram of graphite is burned the same weight ($3\frac{2}{3}$ grams) of carbon dioxide is obtained as in the case of charcoal; and the same thing is true of diamond. It follows from these facts that the three forms of matter known as charcoal, graphite, and diamond consist only of the element carbon. The explanation of the difference is not known, but, as in the cases of phosphorus and sulphur, it will probably be found to be in the different ways in which the atoms are arranged in the molecule, and the molecules in the masses.

Notwithstanding the marked differences in their appearance and in many of their physical properties, the three forms of carbon have, as we have seen, some properties in common. They are insoluble in all known liquids at ordinary temperatures. They are tasteless, inodorous, and infusible. When heated without access of air they remain unchanged, unless the temperature is very high, when the diamond swells up and is converted into a mass resembling coke—a change which is connected with a rearrangement of the particles in an irregular way, so that the substances cease to be crystalline, or become amorphous.

**Chemical Conduct of Carbon.**—At ordinary temperatures carbon is an inactive element. If it is left in contact with any one of the elements, no chemical change takes place. It will not combine with any of them unless the temperature is raised. At higher temperatures, however, it combines with several of them with great ease, especially with oxygen. Under proper conditions it combines also with nitrogen, with hydrogen, with sulphur, and with many other elements. It combines with oxygen either directly, as when it burns in the air or in oxygen; or it abstracts oxygen from some of the oxides. The direct combination of oxygen and carbon has already been seen in the burning of charcoal in oxygen, and is familiar to every one in the fire in a charcoal furnace. That car-

bon dioxide is the product formed can be shown by passing the gas through lime-water or baryta-water, when insoluble calcium or barium carbonate will be thrown down. The reason why lime-water or baryta-water is used is simply that an insoluble compound is formed, and this can be seen, and it can be separated from the liquid and examined. The reaction which takes place is represented thus:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O;$$

Calcium hydroxide    Carbon dioxide    Calcium carbonate

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

Barium hydroxide    Carbon dioxide    Barium carbonate

No other common gas acts in this way on these solutions. Hence, when, under ordinary circumstances, a gas is passed into lime-water and an insoluble compound is formed, we may conclude that the gas is carbon dioxide, though this conclusion may require further proof.

The abstraction of oxygen from compounds by means of carbon may be illustrated in a number of ways. Thus, when powdered copper oxide, $CuO$, is mixed with powdered charcoal, and the mixture heated in a tube, carbon dioxide is given off, and can be detected as in the last experiment mentioned. Copper is left behind, and, if the proportions are properly selected, all the carbon will pass off as carbon dioxide, and only the copper be left behind:

$$2CuO + C = 2Cu + CO_2.$$

In a similar way, arsenious oxide, $As_2O_3$, gives up its oxygen to carbon. This fact furnishes indeed a delicate method for the detection of the substance. If a little is placed in the bottom of a small tube, and above it a small piece of charcoal, then when heat is applied the arsenious oxide sublimes, and as its vapor passes the heated charcoal the oxygen is abstracted, and the element arsenic, being also somewhat volatile, is deposited

just above the charcoal in the form of a lustrous mirror on the walls of the tube. The reaction is

$$2As_2O_3 + 3C = 4As + 3CO_2.$$

As has already been explained, the abstraction of oxygen from a compound is known as *reduction.* Hence, carbon is called a reducing agent. It is indeed the reducing agent which is most extensively used in the arts. Its chief use is in extracting metals from their ores, which are the forms in which they occur in nature. Thus, iron does not occur in nature as iron, but in combination with other elements, especially with oxygen. In order to get the metal the ore must be reduced, or, in other words, the oxygen must be extracted. This is invariably accomplished by heating it with some form of carbon, either coke or charcoal.

The elements chlorine, oxygen, nitrogen, and hydrogen being gases, and the products formed when the first three combine with hydrogen being also gaseous or convertible into vapor, it is a comparatively easy matter to study the relations between the volumes of the combining gases and the volumes of the products formed. It is, however, impossible to determine the ratio between the volume of carbon gas and that of other gases with which it combines.

**Compounds of Carbon with Hydrogen, or Hydrocarbons. Conditions under which Hydrocarbons are Formed.**—When the carbon pencils connected with a powerful battery, as in the production of the electric arc-light, are surrounded by an atmosphere of hydrogen the two elements combine to some extent to form the compound acetylene, $C_2H_2$. When organic matter undergoes decomposition without free access of air, as for example under water, the carbon compounds are reduced to the final product known as marsh-gas or methane, $CH_4$, just as compounds containing nitrogen yield ammonia. Compounds of various metals with carbon, known as *carbides*, yield hydrocarbons, such as acetylene and marsh-gas, when treated with water. The compounds which make up petroleum are hydrocarbons which have probably been

formed, either by the action of water on metallic carbides in the interior of the earth, or by decomposition of organic matter without free access of air. Finally, when wood or coal is heated, hydrocarbons are given off, and compounds of this kind are therefore contained in coal-gas.

**Number of Hydrocarbons.**—The number of hydrocarbons is very great, and new ones are constantly being made. The fact that carbon is distinguished for the large number of its compounds has already been mentioned. The simplest of these are the hydrocarbons. It is safe to say that there are as many as two hundred hydrocarbons known. Fortunately, however, most of these have been found to bear comparatively simple relations to one another, and therefore, though the number is large and the variety great, their study is not as difficult as one would be inclined to think.

*Petroleum* is an oily liquid found in many places in the earth in large quantity, and escapes when a cavity in which it is contained is punctured. In the earth it contains both gases and liquids. When it is brought into the air the gases and the liquids which are volatile at the ordinary temperature are given off. There are several gases given off, and a large number of liquids left behind. The simplest gas corresponds to the formula $CH_4$, the next to $C_2H_6$, the next to $C_3H_8$, the next to $C_4H_{10}$. An examination of the liquid has shown that it contains other hydrocarbons of the formulas $C_5H_{12}$, $C_6H_{14}$, $C_7H_{16}$, $C_8H_{18}$, etc. It will be seen that these compounds bear a simple relation to one another, as far as composition is concerned. Arranging them in a series, the first eight members are

$CH_4$,    Methane, or Marsh-gas ;
$C_2H_6$,    Ethane ;
$C_3H_8$,    Propane ;
$C_4H_{10}$,    Butane ;
$C_5H_{12}$,    Pentane ;
$C_6H_{14}$,    Hexane ;
$C_7H_{16}$,    Heptane ;
$C_8H_{18}$,    Octane.

**Homology, Homologous Series.**—In the above series the first member differs from the second by $CH_2$; and there is also this same difference between the second and third, the third and fourth, and in general between any two consecutive members in the series. This relation is known as *homology*, and such a series is known as an *homologous series*. Carbon is distinguished from all other elements by its power to form homologous series. Other elements form similar series, but the homology is not of the same kind as that which is met with among carbon compounds. Thus the series of chlorine acids, and the similar series of acids of nitrogen and sulphur, are homologous series, in which the constant difference between any two consecutive members is represented by an atom of oxygen:

$$HClO \qquad\qquad H_2SO_2 \qquad\qquad HNO$$
$$HClO_2 \qquad\qquad H_2SO_3 \qquad\qquad HNO_2$$
$$HClO_3 \qquad\qquad H_2SO_4 \qquad\qquad HNO_3.$$
$$HClO_4$$

These series, are, however, much less extensive than the homologous series of compounds of carbon.

**Cause of the Homology among Compounds of Carbon.**—The explanation of the homology observed between the compounds of carbon is founded on the view that carbon is quadrivalent, and that it has the power to unite with itself in chains. The quadrivalence is shown in the compounds $CH_4$, $CCl_4$, $CHCl_3$, $CO_2$, etc. When marsh-gas, $CH_4$, is treated with chlorine the first product of the action is chlor-methane, $CH_3Cl$, which according to the prevailing views is marsh-gas in whose molecule one atom of hydrogen has been replaced by chlorine. The structure of this compound is represented thus, $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Cl$,

if that of marsh-gas is represented in this way, $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$.

Now, when chlor-methane is treated with sodium the chlorine is extracted, and a compound of the formula $C_2H_6$ is formed:

$$2CH_3Cl + 2Na = C_2H_6 + 2NaCl.$$

It appears that, the chlorine being extracted from the compound, the residues of the composition $CH_3$ unite in pairs to form the compound $C_2H_6$, which is ethane, or the second member of the series of hydrocarbons above given. The simplest explanation of the facts stated is that the carbon atoms unite by means of the bonds or valences left free when the chlorine is extracted. The residues after the extraction of the chlorine may be rep-

resented by the formula $H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$; when two of these

unite, the resulting compound will have the structure represented by the formula $H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$. In a similar

way the relation between the other members of the series can be explained, and the explanation is in perfect accordance with a large number of facts.

**Other Series of Hydrocarbons.**—Besides the series above mentioned, which, as its simplest member is marsh-gas, is known as the *marsh-gas series*, there are other homologous series of hydrocarbons. There is one beginning with ethylene, or olefiant gas, $C_2H_4$, examples of which are

Ethylene,  $C_2H_4$ ;
Propylene, $C_3H_6$ ;
Butylene,  $C_4H_8$.

There is another beginning with acetylene, $C_2H_2$, examples of which are

Acetylene,  $C_2H_2$ ;
Allylene,   $C_3H_4$.

Another series begins with benzene, $C_6H_6$. Some of the members of this series are

Benzene, $C_6H_6$;
Toluene, $C_7H_8$;
Xylene, $C_8H_{10}$.

These are the hydrocarbons which are obtained from coal-tar.

The relations between these hydrocarbons and those of the marsh-gas series have been extensively studied, and a great deal of light has been thrown upon the subject. It would, however, lead too far to take up this subject here. A word may be said, however, in regard to the relations believed to exist between the hydrocarbons of the ethylene and the acetylene series, and those of the marsh-gas series. It is believed that in ethylene the two carbon atoms are united in a different way from that in ethane. The condition, whatever it may be, is thought to be similar to that which exists in the molecule of a compound consisting of two bivalent atoms, as, for example, calcium oxide. The condition is called double union, and it is represented by a double line as in the formulas $Ca=O$, $H_2C=CH_2$, etc. Whatever this condition may be, it carries with it the power to combine with other atoms. Thus, when ethylene is treated with chlorine it takes up two atoms, and is converted into dichlorethane, $C_2H_4Cl_2$, the double union being destroyed and single union existing in the resulting compound as in ethane. So also, when calcium oxide, $Ca=O$, is treated with water, it is converted into the hydroxide, in which the condition of double union does not exist:

$$\begin{matrix} Ca \\ \| \\ O \end{matrix} + \begin{matrix} OH \\ | \\ H \end{matrix} = \begin{matrix} Ca-OH \\ | \\ OH \end{matrix} ;$$

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} Cl \\ | \\ Cl \end{matrix} = \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} .$$

Similar reasons have led to the conclusion that in acetylene, $C_2H_2$, the carbon atoms are held together in

a different way from that in ethane, and that in ethy-
lene. This is believed to be similar to the kind of union
which exists in a molecule consisting of two trivalent
atoms, as in the compound boron nitride, $B\equiv N$, a con-
dition which is called triple union or triple linkage. This
view is expressed by the formula $HC\equiv CH$. Wherever
this condition exists we find the power to take up four
univalent atoms, the compound thus becoming saturated,
as we say. Thus, acetylene can take up four atoms of
chlorine, or two of hydrogen and two of chlorine, form-
ing in the former case tetra-chlor-ethane, and in the latter
di-chlor-ethane:

$$HC\equiv CH + 4Cl = Cl_2HC-CHCl_2(C_2H_2Cl_4);$$
$$HC\equiv CH + 2HCl = ClH_2C-CH_2Cl(C_2H_4Cl_2).$$

**Marsh-gas, Methane, Fire-damp, $CH_4$.**—Marsh-gas is
found in nature in petroleum, and is given off when the
oil is taken out of the earth and the pressure removed.
It is formed, as the name implies, in marshes, as the
product of a reducing process. Vegetable matter is com-
posed essentially of carbon, hydrogen, and oxygen.
When it undergoes decomposition in the air in a free
supply of oxygen, the final products formed are carbon
dioxide and water. When the decomposition takes
place without access of oxygen, as under water, marsh-
gas, which is a reduction-product, is formed. The gas
can be made in the laboratory by passing a mixture of
hydrogen sulphide and the vapor of carbon disulphide
**over heated** copper, and also by the action of water on
several metallic carbides, more especially aluminium
carbide, $C_3Al_4$:

$$C_3Al_4 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

The gas is met with in coal-mines, and is known to
the miners as *fire-damp,* damp being the general name
applied to a gas, and the name fire-damp meaning a gas
that burns. To prepare it in the laboratory it is most
convenient to heat a mixture of sodium acetate and

quick-lime. The change which takes place will be most readily understood by regarding it as a simple decomposition of acetic acid. Acetic acid has the formula $C_2H_4O_2$. When heated alone it boils, and does not suffer decomposition. If it is converted into a salt, and heated in the presence of a base, it breaks down into marsh-gas and carbon dioxide:

$$C_2H_4O_2 = CH_4 + CO_2.$$

The carbon dioxide, which with bases forms salts, does not pass off, but remains behind in the form of a salt of carbonic acid.

Marsh-gas is a colorless, transparent, tasteless, inodorous gas. It is slightly soluble in water, and burns, forming carbon dioxide and water. When mixed with air the mixture explodes if a flame or spark comes in contact with it. This is one of the causes of the explosions which so frequently occur in coal-mines. To prevent these explosions a special lamp was invented by Sir Humphry Davy, which is known as the *safety-lamp*. The simple principles involved in its construction will be explained when the subject of *flame* is taken up.

**Ethylene, Olefiant Gas, $C_2H_4$.**—This hydrocarbon is formed by heating a mixture of ordinary alcohol and concentrated sulphuric acid. The reaction is represented thus:

$$C_2H_6O = H_2O + C_2H_4.$$
$$\text{Alcohol} \qquad\qquad \text{Ethylene}$$

Ethylene is a colorless gas, which can be condensed to a liquid. It burns with a luminous flame, and forms an explosive mixture with oxygen.

**Acetylene, $C_2H_2$.**—Acetylene is formed when a current of hydrogen is passed between carbon poles, which are incandescent in consequence of the passage of a powerful electric current. In this case carbon and hydrogen combine directly. It is formed also when the flame of an ordinary laboratory gas-burner (Bunsen burner) "strikes back," or burns at the base without a free sup-

ply of air. It is most easily obtained by treating certain metallic carbides, especially calcium carbide, with water:

$$C_2Ca + H_2O = C_2H_2 + CaO.$$

Its odor is unpleasant. It burns with a luminous, smoky flame.

**Simpler Compounds of Carbon with the Members of the Chlorine Group.**—When chlorine acts upon a hydrocarbon it generally takes the place of the hydrogen, atom for atom. Thus, when it acts upon marsh-gas, the following reactions take place:

$$CH_4 \quad + Cl_2 = CH_3Cl \quad + HCl;$$
$$CH_3Cl \quad + Cl_2 = CH_2Cl_2 + HCl;$$
$$CH_2Cl_2 + Cl_2 = CHCl_3 \quad + HCl;$$
$$CHCl_3 + Cl_2 = CCl_4 \quad \quad + HCl.$$

The four products are known respectively as *mono-chlor-methane, di-chlor-methane, tri-chlor-methane,* and *tetra-chlor-methane,* or *carbon tetrachloride.* By treating these compounds with nascent hydrogen they can all be converted back again into marsh-gas. The fact that the hydrogen in marsh-gas can be replaced in four steps, one fourth of the hydrogen being replaced at each step, furnishes a strong confirmation of the correctness of the view expressed by the formula $CH_4$, which signifies that in the molecule of marsh-gas there are four atoms of hydrogen. The most important of the four compounds is the third, tri-chlor-methane or *chloroform.* While chloroform can be made by treating marsh-gas with chlorine, it is much more easily obtained in other ways, as, for example, by treating alcohol or acetone with bleaching-powder. Without a study of the relations which exist between several classes of compounds of carbon these reactions cannot well be explained, and their study, as well as that of chloroform, had better be postponed until the subject of Organic Chemistry is taken up systematically. Corresponding to chloroform there are bromine and iodine derivatives, known as *bromoform,* $CHBr_3$, and *iodoform,* $CHI_3$.

# CHAPTER XX.

**General.**—The final product of oxidation of carbon is
carbon dioxide, and the final product of reduction is
marsh-gas, but between these two limits there are a
number of interesting derivatives, just as there are a
number of compounds of sulphur between hydrogen sul-
phide and sulphuric acid; a number of compounds of
nitrogen between ammonia and nitric acid; and a number
of compounds of phosphorus between phosphine and
phosphoric acid. We have seen that in the cases men-
tioned two kinds of change are brought about by oxida-
tion: (1) Owing to the fact that the valence of chlo-
rine, sulphur, nitrogen, and phosphorus towards oxygen
is greater than towards hydrogen, the act of oxidation
involves the addition of oxygen to the element; (2) **hy-
droxyl appears to take the place of the hydrogen atoms
one by one.** In the case of carbon, the valence towards
hydrogen and oxygen being the same, only the latter
kind of change takes place.

**Relations between the Compounds of Carbon with Hy-
drogen and Oxygen.**—In order that the relations between
the simpler compounds of carbon with hydrogen and
oxygen may be made clear, it will be of assistance to
compare the oxidation of hydrogen sulphide, ammonia,
phosphine, and methane. In the cases of hydrogen sul-
phide and ammonia the oxidation appears to take place
as represented below:

$$S \left\{ \begin{matrix} H \\ H \end{matrix} \right. , \quad O_2S \left\{ \begin{matrix} H \\ H \end{matrix} \right. , \quad O_2S \left\{ \begin{matrix} OH \\ H \end{matrix} \right. , \quad O_2S \left\{ \begin{matrix} OH \\ OH \end{matrix} \right. ;$$

Hydrogen          Unknown          Sulphurous          Sulphuric
Sulphide                            acid                acid
(376)

$$N\begin{cases} H \\ H, \\ H \end{cases} \quad N\begin{cases} OH \\ H \\ H \end{cases}, \quad N\begin{cases} OH \\ OH, \\ H \end{cases} \quad N\begin{cases} OH \\ OH, \\ OH \end{cases} \quad ON\begin{cases} OH \\ OH. \\ OH \end{cases}$$

| Ammonia | Hydroxyl-amine | Yields hypo-nitrous acid | Yields nitrous acid | Yields nitric acid |

The last three products, if formed, break down, losing water, and forming respectively hyponitrous, nitrous, and nitric acids. The change to hyponitrous acid does not appear to be of an altogether simple kind. The changes to nitrous and nitric acids, however, are apparently of a kind which we are constantly meeting with, as has already been pointed out (see pp. 261–265).

It is possible that the changes involved in the gradual oxidation of ammonia take place primarily just as in the oxidation of sulphur, the nitrogen first becoming saturated. According to this view the changes should be represented as follows :

$$N\begin{cases} H \\ H, \\ H \end{cases} \quad ON\begin{cases} H \\ H, \\ H \end{cases} \quad ON\begin{cases} OH \\ H \\ H \end{cases}, \quad ON\begin{cases} OH \\ OH, \\ H \end{cases} \quad ON\begin{cases} OH \\ OH. \\ OH \end{cases}$$

If nitrous acid were formed by the breaking down of the compound $ON\begin{cases} OH \\ OH \\ H \end{cases}$, its structure would probably

be that represented by the formula $N\begin{cases} O \\ O, \\ H \end{cases}$ or $O_2NH$,

the hydrogen being in combination with nitrogen and not with oxygen. Some facts seem to show that this view is probable. While these changes cannot be followed very well in the case of the compounds of nitrogen, and there is, therefore, considerable speculation in what has just been said regarding them, the case of phosphorus is much clearer, as has already been shown. Here, starting with phosphine, the changes are apparently correctly represented by the following formulas :

$$P\begin{Bmatrix} H \\ H \\ H \end{Bmatrix}, \quad OP\begin{Bmatrix} H \\ H \\ H \end{Bmatrix}, \quad OP\begin{Bmatrix} OH \\ H \\ H \end{Bmatrix}, \quad OP\begin{Bmatrix} OH \\ OH \\ H \end{Bmatrix}, \quad OP\begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix}.$$

Phosphine     Unknown     Hypophosphor-     Phosphorous     Phosphoric
                         ous acid          acid          acid

With methane the changes effected by oxidation are apparently perfectly analogous to those considered. We should expect to find the following:

$$C\begin{bmatrix} H \\ H \\ H \\ H \end{bmatrix}, \quad C\begin{bmatrix} H \\ H \\ H \\ OH \end{bmatrix}, \quad C\begin{bmatrix} H \\ H \\ OH \\ OH \end{bmatrix}, \quad C\begin{bmatrix} H \\ OH \\ OH \\ OH \end{bmatrix}, \quad C\begin{bmatrix} OH \\ OH \\ OH \\ OH \end{bmatrix}.$$

$$\quad 1 \qquad\qquad 2 \qquad\qquad 3 \qquad\qquad 4 \qquad\qquad 5$$

But the tendency of the compounds containing two hydroxyl groups to break down, yielding water as one of the products, is as marked as in the compounds of nitrogen. Consequently the products 3, 4, and 5 do not exist in the free state. They break down as represented in the following equations:

$$C\begin{bmatrix} H \\ H \\ OH \\ OH \end{bmatrix} = C\begin{Bmatrix} H \\ H \\ O \end{Bmatrix} + H_2O;$$

$$C\begin{bmatrix} H \\ OH \\ OH \\ OH \end{bmatrix} = C\begin{Bmatrix} H \\ O \\ OH \end{Bmatrix} + H_2O;$$

$$C\begin{bmatrix} OH \\ OH \\ OH \\ OH \end{bmatrix} = C\begin{Bmatrix} O \\ O \end{Bmatrix} + 2H_2O.$$

The products actually obtained, therefore, are as follow:

$$C\begin{cases} H \\ H \\ H \\ H \end{cases}, \quad C\begin{cases} H \\ H \\ H \\ OH \end{cases}, \quad C\begin{cases} H \\ H \\ O \end{cases}, \quad C\begin{cases} H \\ O \\ OH \end{cases}, \quad C\begin{cases} O \\ O \end{cases}.$$

Methane     Methyl     Formic     Formic     Carbon
          alcohol    aldehyde    acid     dioxide

By oxidation of formic acid we should expect the formation of a product, $C\begin{cases} OH \\ O \\ OH \end{cases}$. While this is not known, salts of an acid of this composition are known. It is ordinary carbonic acid, which when set free breaks down into carbon dioxide and water.

It will be seen from the above considerations that there is a general analogy between the changes which take place in passing by oxidation from the lowest reduction-products of the elements to their highest oxidation-products.

The intermediate stages have been studied with special care in the case of carbon ; the intermediate products represent classes of compounds which are not met with among any derivatives of the other elements. The intermediate products in the case of sulphur and phosphorus are all acids. One of the intermediate products in the case of nitrogen, hydroxylamine, is basic, while the rest are acid. The first oxidation-product of marsh-gas, *methyl alcohol*, $CH_3.OH$, is somewhat basic, but in some respects differs from ordinary bases. It is the simplest representative of a great class of compounds of carbon known as *alcohols*, of which our ordinary alcohol, or spirits of wine, is the best known example. The next product, or *formic aldehyde*, which has the structure represented by the formula $C\begin{cases} H \\ H \\ O \end{cases}$ or $H_2C=O$, is the simplest representative of another great class of compounds of carbon known as *aldehydes*. The aldehydes are neither acid nor basic, but are easily converted into acids by oxidation, and into bases

by reduction. The third oxidation-product of the formula

$$C \begin{cases} H \\ OH \\ O \end{cases} \quad \text{or} \quad O = \overset{\displaystyle H}{\underset{\displaystyle OH}{C}}$$ is the simplest representative of a

great class of carbon compounds known as the *organic acids*. It is called *formic acid*. It would lead too far to pursue this subject now. The relations referred to are studied under the head of Organic Chemistry, or the Chemistry of the Compounds of Carbon. Only the simplest oxygen compounds will be taken up here.

**Carbon Dioxide, $CO_2$.**—The principal compound of carbon and oxygen is carbon dioxide, $CO_2$, commonly known as *carbonic acid gas*. Under the head of The Air attention was called to the fact that this gas is a constant constituent of the air, though its relative quantity is small— about 3 parts in 10,000. It issues from the earth in many places, particularly in the neighborhood of volcanoes. Many mineral waters contain it in large quantity, prominent among which are the waters of Pyrmont, Selters, and the Geyser Spring of Saratoga. In small quantity it is present in all natural waters. In combination with bases it occurs in enormous quantities, particularly in the form of calcium carbonate, $CaCO_3$, varieties of which are ordinary limestone, chalk, marble, and calc-spar. Dolomite, which forms mountain-ranges, being particularly abundant in the Swiss Alps, is a compound containing calcium carbonate and magnesium carbonate, $MgCO_3$.

Carbon dioxide is constantly formed in many natural processes. Thus, all animals that breathe in the air give off carbon dioxide from the lungs. That the gases from the lungs contain carbon dioxide can easily be shown by passing them through lime-water, when a precipitate of calcium carbonate is formed.

That carbon dioxide is formed in the combustion of charcoal and wood has already been shown. In a similar way it can be shown that the gas is formed whenever any of our ordinary combustible substances are burned. From our fires, as from our lungs, and from the lungs of all animals, then, carbon dioxide is constantly given off.

Further, the natural processes of decay of both vegetable and animal matter tend to convert the carbon of this matter into carbon dioxide, which then finds its way principally into the air. The process of alcoholic fermentation, and some other similar processes, also give rise to the formation of carbon dioxide. In all fruit-juices there is contained sugar. When the fruits ripen, fall to the earth, and undergo spontaneous change, the sugar is converted into alcohol and carbon dioxide. We see, thus, that there are many important sources of supply of carbon dioxide, and it will be readily understood why the gas should be found everywhere in the air.

**Preparation.**—The easiest way to get carbon dioxide not mixed with other substances is by adding an acid to a salt of carbonic acid or a carbonate. In the decomposition of the carbonates by other acids we see exemplified the same principle as that which is involved in setting nitric acid free from a nitrate, or hydrochloric acid from sodium chloride by sulphuric acid, and more particularly in the liberation of sulphur dioxide from a sulphite. In all these cases the products are volatile, and therefore, when a non-volatile acid is added to the salts, decomposition takes place. Sulphites do not yield the corresponding acid, but this breaks down into water and the anhydride:

$$\begin{cases} 2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3\,; \\ 2NaCl \ \ + H_2SO_4 = Na_2SO_4 + 2HCl. \end{cases}$$

$$\begin{cases} Na_2SO_3 \ + H_2SO_4 = Na_2SO_4 + H_2SO_3\,; \\ H_2SO_3 \ \ = SO_2 \ \ + H_2O. \end{cases}$$

$$\begin{cases} Na_2CO_3 \ + H_2SO_4 = Na_2SO_4 + H_2CO_3\,; \\ H_2CO_3 \ \ = CO_2 \ \ + H_2O. \end{cases}$$

Any acid which is not volatile at the ordinary temperature will decompose a carbonate and cause an evolution of carbon dioxide. The action between sodium carbonate and hydrochloric acid is represented in this way:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O\,;$$

that between nitric acid and sodium carbonate in this way:

$$Na_2CO_3 + 2HNO_3 = 2NaNO_3 + CO_2 + H_2O.$$

For the purpose of preparing carbon dioxide in the laboratory, calcium carbonate, in the form of marble or limestone, and hydrochloric acid are commonly used. The reaction involved is represented thus:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

The apparatus used is the same as that used in making hydrogen from zinc and sulphuric acid. As the gas is somewhat soluble in water, it is best for ordinary purposes to collect it by displacement of air, the vessel being placed with the mouth upward, as the gas is considerably heavier than air.

**Properties.**—Carbon dioxide is a colorless gas at ordinary temperatures. When subjected to a low temperature and high pressure it is converted into a liquid. Liquid carbon dioxide is now manufactured on the large scale for use as a fire-extinguisher, and for the purpose of charging liquids with the gas. When some of the liquid is exposed to the air evaporation takes place so rapidly that a great deal of heat is absorbed, and some of the liquid becomes solid. The gas has a slightly acid taste and smell. It is not combustible, nor does it support combustion. It is not combustible for the same reason that water is not: because it already holds in combination all the oxygen it has the power to combine with. Before it can burn again it must first be decomposed. As regards the statement that it does not support combustion, it should be remarked that this is only relatively true. The compound does not easily give up oxygen, but to some substances it does give it up, and some such substances burn in it. For example, the element potassium, which, as we have seen, has the power to decompose water, has also the power to decompose carbon dioxide if heated in it to a sufficiently high temperature, and when the decomposition once begins, it

proceeds with brilliancy, the act being accompanied by a marked evolution of heat and light. Carbon dioxide is much heavier than air, its specific gravity being 1.529. A liter of the gas under standard conditions of temperature and pressure weighs 1.977 grams. It dissolves in water, one volume of water dissolving about one volume of the gas at the ordinary temperature. As is the case with all gases, when the pressure is increased the water dissolves more gas, and when the pressure is removed the gas again escapes. The so-called "soda-water" is simply water charged with carbon dioxide under pressure. The escape of the gas when the water is drawn is familiar to every one. The name soda-water has its origin in the fact that the carbon dioxide used in charging the water is frequently made from primary or acid sodium carbonate, $NaHCO_3$, which is also called soda or bicarbonate of soda.

**Relations of Carbon Dioxide to Chemical Energy.—** Carbon has the power to combine with oxygen, and in so doing a definite quantity of heat is evolved. A kilogram of carbon represents a certain quantity of chemical energy, which we can get from it first in the form of heat, and by transformation, in other forms of energy, as motion, electrical energy, etc. After the kilogram of carbon has been burned it no longer represents the energy it did in the form of carbon. A body of water elevated ten or fifteen feet represents a certain quantity of energy which can be obtained by allowing the water to fall upon the paddles of a water-wheel connected with the machinery of a mill. After the water has fallen, however, it no longer has the power to do work, or it has none of the energy which it possessed by virtue of its position. In order that it may again do work it must again be lifted. So, too, in order that the carbon in carbon dioxide may again do work the compound must be decomposed.

**Respiration.—** It was stated above that carbon dioxide is given off from the lungs just as it is from a fire. It is a waste-product of the processes taking place in the animal body. Just as it cannot support combustion, so also it cannot support respiration. It is not poisonous any

more than water is ; but it is not able to supply the oxygen which is needed for breathing purposes, and hence animals die when placed in it. They die by suffocation, very much as they do in drowning. Any considerable increase in the quantity of carbon dioxide in the air above that which is normally present is objectionable, for the reason that it decreases the proportion of oxygen in the air which is breathed. If, however, pure carbon dioxide is introduced into the air, it has been found that as much as 5 per cent may be present without serious results to those who breathe it. In a badly ventilated room in which a number of people are collected, and lights are burning, it is well known that in a short time the air becomes foul, and bad effects, such as headache, drowsiness, etc., are produced on the occupants of the room. These effects appear to be due, not to the carbon dioxide, but largely to other waste-products which are given off from the lungs in the process of breathing. The gases given off from the lungs consist of nitrogen, oxygen, carbon dioxide, and water vapor. Besides these, however, there are many substances in small quantity, in a finely divided condition, which contain carbon, and are in a state of decomposition. These act as poisons, and they are the chief cause of the bad effects experienced in breathing air which is contaminated by the exhalations from the lungs. As carbon dioxide is given off from the lungs at the same time, the quantity of this gas present is proportional to the quantity of the organic impurities. Hence, by determining the quantity of carbon dioxide it is possible to form an opinion as to whether the air of a room occupied by human beings is fit for use or not.

As carbon dioxide is formed in the earth wherever an acid solution comes in contact with a carbonate, the gas is frequently given off from fissures in the earth. It is hence not unfrequently found in old wells which have not been in use for some time, and deaths have been caused by descending these wells for the purpose of repairing them. The gas is also frequently met with in mines, and is called *choke-damp* by the miners. The miners are

aware that after an explosion caused by fire-damp there is danger of death from choke-damp. The reason of the presence of this gas after an explosion is simple. When fire-damp, or marsh-gas, explodes with air the carbon is oxidized to choke-damp, or carbon dioxide, and the hydrogen to water. Air in which a candle will not burn is not fit for breathing purposes.

**Carbon Dioxide and Life.**—The *rôle* played by carbon dioxide in nature is extremely important and interesting. The carbon contained in living things is obtained from carbon dioxide, and generally returns to this form when life ceases. We have seen that all living things contain carbon as an essential constituent. Whence comes this carbon? Animals eat either the products of plant-life or other animals which derive their sustenance from the vegetable kingdom. The food of animals comes, then, either directly or indirectly from plants. But plants derive their sustenance largely from the carbon dioxide of the air. The plants have the power to decompose the gas with the aid of the direct light of the sun, and they then build up the complex compounds of carbon which form their tissues, using for this purpose the carbon of the carbon dioxide which they decompose. Many of these compounds are fit for food for animals; that is to say, they are of such composition that the forces at work in the animal body are capable of transforming them into animal tissues, or of oxidizing them, and thus keeping the temperature of the body up to the necessary point. That part of the food which undergoes oxidation in the body plays the same part as fuel in a stove. It is burned up with an evolution of heat, the carbon being converted into carbon dioxide, which is given off from the lungs. From fires and from living animals carbon dioxide is returned to the air, where it again serves as food for plants. When the life process stops in the animal or the plant, decomposition begins; and the final result of this, under ordinary circumstances, is the conversion of the carbon into the dioxide.

**Energy Stored up in Plants.**—It will thus be seen that under the influence of life and sunlight carbon dioxide is

constantly being converted into compounds containing carbon which are stored up in the plant. These compounds are capable of burning, and thus giving heat; or some of them may be used as food by animals, when they assume other forms under the influence of the life-process of the animals. As long as life continues, plants and animals are storehouses of energy. When death occurs, the carbon compounds begin to pass back to the form of carbon dioxide, and the chemical energy is transformed partly into heat, and is thus, as we say, dissipated. The power to do work, which the carbon compounds of plants and animals possess, comes from the heat of the sun. It takes a certain quantity of this heat, operating under proper conditions, to decompose a certain quantity of carbon dioxide, and elaborate the compounds contained in the plants. When these compounds are burned they give out the heat which was absorbed in their formation during the growth of the plants. These compounds are said to possess chemical energy. This has its origin in heat, and is capable of reconversion into heat. The transformation of the energy of the sun's heat into chemical energy lies at the foundation of all life. As the heat of the sun acting upon the great bodies of water and on the air gives rise to the movements of water which are so essential to the existence of the world as it is, so the action of the sun's rays on carbon dioxide, under the influence of the delicate and inexplicable mechanism of the leaf of the plant, gives rise to those changes in the forms of combination of the element carbon which accompany and are fundamental to the wonderful process of life.

**Carbonic Acid and Carbonates.**—When carbon dioxide is passed into water the solution has a slightly acid reaction. The solution will act upon bases and form salts. The formula of the sodium salt formed in this way has been shown to be $Na_2CO_3$; that of the potassium salt, $K_2CO_3$; etc. These salts are plainly derived from an acid, $H_2CO_3$, which is called carbonic acid. It is probable that this acid is contained in the solution of carbon

dioxide in water. It is, however, so unstable that it breaks up into carbon dioxide and water:

$$H_2CO_3 = CO_2 + H_2O.$$

The formation of a salt by the action of carbon dioxide on a base takes place as shown in the following equations:

$$2KOH \ + CO_2 = K_2CO_3 + H_2O\,;$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

With the acid the action would take place as represented thus:

$$2KOH \ + H_2CO_3 = K_2CO_3 + 2H_2O\,;$$
$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O.$$

There is perfect analogy between the action of carbon dioxide and that of sulphur dioxide on basic solutions. With potassium hydroxide and calcium hydroxide, sulphur dioxide acts as represented in the following equations:

$$2KOH \ + SO_2 = K_2SO_3 + H_2O\,;$$
$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O.$$

The products formed are sulphites or salts of sulphurous acid.

Like sulphurous acid, carbonic acid is dibasic, and forms two series of salts, the *primary* and *secondary*, or the *acid* and *normal salts*. The primary or acid salts have the general formula $HMCO_3$, and the secondary or normal salts have the general formula $M_2CO_3$. Examples of the former are $HKCO_3$, $HNaCO_3$, $CaH_2(CO_3)_2$, etc.; and of the latter $K_2CO_3$, $Na_2CO_3$, $CaCO_3$, $BaCO_3$, etc. It also readily forms basic salts, as, for example, basic copper carbonate. Neutral copper carbonate is to be regarded as formed by the action of one molecule of the dibasic carbonic acid upon one molecule of the diacid copper hydroxide, $Cu(OH)_2$:

$$OC{<}^{OH}_{OH} + {}^{HO}_{HO}{>}Cu = OC{<}^{O}_{O}{>}Cu + 2H_2O.$$

One of the simplest basic carbonates of copper is that formed by the action of two molecules of copper hydroxide upon one molecule of carbonic acid:

$$OC{<}^{OH}_{OH} + {}^{(HO)Cu(OH)}_{(HO)Cu(OH)} = OC{<}^{OCuOH}_{OCuOH} + 2H_2O.$$

Another basic salt of more complicated composition is that of magnesium. It is to be regarded as derived from carbonic acid as represented in this formula:

$$\begin{matrix} CO{<}^{OMgOH}_{O_2Mg} \\ CO{<}^{}_{O_2Mg} \\ CO{<}^{}_{OMgOH} \end{matrix}$$

There are some salts which are derived from a pyrocarbonic acid, that is, a form of the acid derived from two molecules of the acid by loss of one molecule of water:

$$2CO{<}^{OH}_{OH} = H_2C_2O_5 + H_2O.$$

Such a salt is formed by loss of water from the primary sodium salt:

$$2HNaCO_3 = Na_2C_2O_5 + H_2O.$$

There are no salts known derived from normal carbonic acid, $C(OH)_4$, though there are some compounds analogous to salts which are derivatives of this normal acid. The secondary or normal salts which carbonic acid forms with the most strongly marked metallic elements, viz., potassium and sodium, are not decomposed by heat, but all other carbonates are decomposed by heat more or less easily, according to the strength of the base. Calcium carbonate when ignited loses carbon dioxide, and lime, or calcium oxide, remains behind:

$$CaCO_3 = CaO + CO_2.$$

**Carbon Monoxide, CO.**—When a substance containing carbon burns in an insufficient supply of air,—as, for example, when the draught in a furnace is not strong enough to remove the products of combustion and supply fresh air,—the oxidation of the carbon is not complete, and the product, instead of being carbon dioxide, is carbon monoxide, CO. This compound can also be made by extracting oxygen from carbon dioxide. It is only necessary to pass the dioxide over heated carbon, when reaction takes place as represented thus :

$$CO_2 + C = 2CO.$$

This method of formation is illustrated in coal fires, and can be well observed in an open grate. The air has free access to the coal, and at the surface complete oxidation takes place. But that part of the carbon dioxide which is formed at the lower part of the grate is drawn up through the heated coal, and is partly reduced to carbon monoxide. When the monoxide escapes from the upper part of the grate it again combines with oxygen, or burns, giving rise to the characteristic blue flame always noticed above a mass of burning anthracite coal. Should anything occur to prevent free access of air, carbon monoxide may readily escape complete oxidation.

The monoxide is also formed by passing steam over highly heated carbon, when this reaction takes place:

$$C + H_2O = CO + H_2.$$

This is the reaction made use of in the manufacture of "water-gas." The gas thus obtained is largely a mixture of hydrogen and carbon monoxide. The gas is enriched by passing it through a furnace in which it is mixed with highly heated vapors of hydrocarbons from petroleum. The main reaction, the decomposition of water by heated carbon, is effected in large furnaces filled with anthracite coal. The coal is first heated to a high temperature by setting fire to it, the products of combustion being allowed to escape. When it is hot enough, the air is

shut off and steam passed rapidly in, when the decom-
position of the water by the carbon takes place. Soon
the mass becomes so much cooled that the reaction
stops. The steam is then cut off and air turned on again,
and so on.

The easiest way to make carbon monoxide is by heat-
ing oxalic acid, which is a compound of carbon, hydro-
gen, and oxygen, of the formula $C_2H_2O_4$, with five to six
times its weight of concentrated sulphuric acid. The
change which takes place is represented thus:

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$

Both the dioxide and monoxide of carbon are formed.
Both are gases. In order to separate them the mixture
is passed through a solution of sodium hydroxide, which
takes up the carbon dioxide, forming sodium carbonate,
and allows the monoxide to pass.

Carbon monoxide is a colorless, tasteless, inodorous
gas, insoluble in water. It burns with a pale-blue flame,
forming carbon dioxide. It is exceedingly poisonous
when inhaled. Hence it is very important that it should
not be allowed to escape into rooms occupied by human
beings. We not unfrequently hear of deaths caused by
the gases from coal stoves. The most dangerous of the
gases given off from these stoves is probably carbon
monoxide. A pan of smouldering charcoal gives off this
gas, and the fact that it is poisonous is well known. It
has been used to a considerable extent for the purpose
of suicide. The poisonous character of carbon monoxide
has led to a great deal of discussion and to some legisla-
tion on the subject of "water-gas." The question has
been repeatedly raised whether government should allow
the manufacture of the gas. There is no doubt of the
fact that it is a dangerous substance, and that it should
not be allowed to escape into the air is obvious. Where-
ever it is used special precautions should be taken to
guard against leaking. There is no doubt that it is
somewhat more poisonous than coal-gas.

At high temperatures carbon monoxide has a very

strong tendency to combine with oxygen, and is hence a good reducing agent. In the reduction of iron from its ores, the carbon monoxide formed in the blast-furnace plays an important part in the reducing process. At ordinary temperatures the gas does not combine readily with oxygen. Thus, it does not act upon ozone, even when heated with it somewhat above the temperature at which ozone is converted into ordinary oxygen. When passed over some substances which are rich in oxygen, as, for example, chromic anhydride, $CrO_3$, and potassium permanganate, $KMnO_4$, in acid solution, it takes up oxygen even at the ordinary temperature. It unites with chlorine in the direct sunlight, and forms the compound known as *carbonyl chloride*, $COCl_2$.

**Formic Acid, $H_2CO_2$.**—Just as carbon dioxide may be regarded as the anhydride of carbonic acid, so carbon monoxide may be regarded as the anhydride of an acid of the formula $H_2CO_2$. While, however, an acid of this formula is known, it is not formed by action of carbon monoxide upon water, nor are its salts easily formed by the action of carbon monoxide upon bases. By passing it over certain basic substances, however, as, for example, potassium hydroxide and calcium hydroxide, at a comparatively high temperature action takes place, and salts of the acid are formed. Thus, in the case of potassium hydroxide, the action takes place as represented in the equation

$$CO + KOH = HCO_2K.$$

Although it contains two atoms of hydrogen in the molecule, formic acid is monobasic. This fact finds its explanation in the structure of the acid. All its reactions show that only one of the hydrogen atoms of formic acid is in combination with oxygen, while the other is in combination with carbon, as represented in the formula

$$\overset{O}{\overset{\|}{H C}}-OH \quad \text{or} \quad C \begin{cases} H \\ O \\ OH \end{cases}$$
. The relations here are similar to

those met with in phosphorous and sulphurous acids,

which have been so frequently referred to. Formic acid bears to carbonic acid the same relation that sulphurous bears to sulphuric acid, and phosphorous to phosphoric acid, as shown in the formulas :

$$OC \begin{cases} H \\ OH \end{cases}$$

Formic acid

$$OC \begin{cases} OH \\ OH \end{cases}$$

Carbonic acid

$$O_2S \begin{cases} H \\ OH \end{cases}$$

Sulphurous acid

$$O_2S \begin{cases} OH \\ OH \end{cases}$$

Sulphuric acid

$$OP \begin{cases} H \\ OH \\ OH \end{cases}$$

Phosphorous acid

$$OP \begin{cases} OH \\ OH \\ OH \end{cases}$$

Phosphoric acid

Formic acid occurs in nature in red ants, in stinging nettles, and elsewhere. It is a colorless liquid, which solidifies at 8°.6. When treated with concentrated sulphuric acid it breaks down into carbon monoxide and water :

$$H_2CO_2 = CO + H_2O.$$

By oxidation it is converted into carbon dioxide and water.

**Carbonyl Chloride, Phosgene, $COCl_2$.**—This compound was referred to above as being formed when chlorine acts upon carbon monoxide under the influence of the sun's rays. It is also formed when the two gases are passed together through a tube filled with pieces of animal charcoal. It is a colorless gas, which is easily condensed to a liquid boiling at 8°.2. It is now manufactured on the large scale for use in the preparation of certain classes of dye-stuffs.

Like the oxychlorides of sulphur and of phosphorus, this compound, which is an oxychloride of carbon, is decomposed by water, forming carbonic acid or its products of decomposition :

$$CO<^{Cl}_{Cl} + ^{HOH}_{HOH} = CO<^{OH}_{OH} + 2HCl;$$

$$SO_2<^{Cl}_{Cl} + ^{HOH}_{HOH} = SO_2<^{OH}_{OH} + 2HCl;$$

$$PO\begin{cases} Cl \\ Cl \\ Cl \end{cases} + \begin{matrix} HOH \\ HOH \\ HOH \end{matrix} = PO\begin{cases} OH \\ OH \\ OH \end{cases} + 3HCl.$$

It is interesting to note that, while the chlorides of sulphur and phosphorus, $SCl_2$ and $PCl_3$, as well as $SCl_4$ and $PCl_5$, are easily decomposed by water, the tetrachloride of carbon, $CCl_4$, is not. On the other hand, the tetrachloride is not formed when the oxides of carbon are treated with hydrochloric acid. It will be remembered that, in discussing the relations between the acid-forming and the base-forming elements, attention was called to the fact that, in general, the chlorides of the acid-forming elements are easily decomposed by water, forming the corresponding hydroxides or oxides, while the oxides and hydroxides of the base-forming elements are converted into chlorides by treatment with hydrochloric acid. In carbon we have an example of an element which occupies what may be called almost a neutral ground between the two classes of elements. It forms both acids and bases, to be sure, but these are, generally speaking, not as strongly marked as the acids and bases formed by other elements. This neutral character of the element is also well shown in the conduct of its chloride towards water, and of its oxides towards hydrochloric acid.

# CHAPTER XXI.

**Introduction.**—As the substances used for illumination contain carbon, and the chemical processes involved consist largely in the oxidation of the carbon of these compounds, this is an appropriate place to consider briefly the subject of illumination from a chemical point of view, as well as that of flame, and the blow-pipe, which gives an extremely useful form of flame constantly used in the laboratory.

In all ordinary kinds of illumination we are dependent upon flames for the light. Whether we use illuminating gas, a lamp, or a candle, the light comes from a flame. In the first case, the gas is burned directly ; in the case of the lamp, the oil is first drawn up the wick, then converted into a gas, and this burns ; while, finally, in the case of the candle, the solid material of the candle is first melted, then drawn up the wick, converted into gas, and the gas burns, forming the flame. In each case we have, then, to deal with a burning gas, and this burning gas is called a flame.

**Illuminating Gas, Coal-gas.**—Illuminating gas is sometimes made from coal by heating in closed retorts. As has already been explained, coal, particularly the softer kinds, contains compounds of carbon and hydrogen, together with some nitrogen and other elements. When it is subjected to destructive distillation, as in the manufacture of coal-gas, the hydrogen passes off partly in combination with carbon, as hydrocarbons, and partly in the free state. The nitrogen passes off as ammonia, and a large percentage of the carbon remains behind in the retort in the uncombined state as *coke*. The gases given

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off are purified, and form illuminating gas. One ton of coal yields on an average 10,000 cubic feet of gas. The value of a gas depends upon the quantity of light given by the burning of a definite quantity. It is measured by comparing it with the light given by a candle burning at a certain rate. The standard candle is one made of spermaceti, which burns at the rate of 120 grains per hour; that is to say, a candle which, burning under ordinary conditions, loses 120 grains in one hour. The standard burner used for the gas is one through which five cubic feet of gas pass per hour. Now, to determine the illuminating power of a gas, it is passed through the standard burner at the rate mentioned, and the light which it gives is compared with the light given by the standard candle. This comparison is easily made by means of an instrument called the *photometer*. The illuminating power of the gas is then stated in terms of the standard candle. The statement that the illuminating power of a gas is fourteen candles, signifies that, when burning at the rate of five cubic feet per hour, its flame gives fourteen times as much light as that of the standard candle.

**Flames.**—Ordinarily when we speak of a flame we mean a gas which is combining with oxygen. The hydrogen flame is simply the phenomenon accompanying the act of combination of the two gases hydrogen and oxygen. Owing to the fact that we are surrounded by oxygen, we speak of hydrogen as the burning gas. How would it be if we were surrounded by an atmosphere of hydrogen? Plainly, oxygen would then be a burning gas. If we allow a jet of oxygen to escape into a vessel containing hydrogen, a flame will appear where the oxygen escapes from the jet, if a light is applied. This is an experiment which requires special precautions, and, as the principle can be illustrated as well by means of illuminating gas, this may be used instead. Just as illuminating gas burns in an atmosphere of oxygen, so oxygen burns in an atmosphere of illuminating gas.

**Kindling Temperature of Gases.**—In studying the action of oxygen upon other substances, we learned that it is

necessary that each of these substances should be raised to a certain temperature before it will combine with oxygen. This statement is as true of gases as of other substances. When a current of hydrogen is allowed to escape into the air, or into oxygen, no action takes place unless it is heated up to its burning temperature, when it takes fire and continues to burn, as the burning of one part of the gas heats up the part which follows it, and hence it is heated up to the burning temperature as fast as it escapes into the air. If the gas is cooled down even very slightly below this temperature, it is extinguished. This can easily be shown by bringing down upon the flame of a Bunsen burner a piece of wire gauze. There will be no flame above the gauze, but gas will pass through unburned, and this will burn if it is lighted above the gauze. In this case, by simply passing through the thin wire gauze, the gases are cooled down below their burning temperatures, and the flame does not pass through. So, also, if the gas is turned on and not lighted, and the gauze held an inch or two above the outlet, the gas will burn above the gauze if lighted above, and will not pass downward through the gauze, unless this becomes very hot.

**Miner's Safety-lamp.**—The principle illustrated in the



Fig. 11.

experiments referred to in the last paragraph is utilized in the miner's *safety-lamp*, to which reference has already been made. One of the dangers which the coal-miner has to encounter is the occurrence in the mines of fire-damp, or methane, $CH_4$, which with air forms an explosive mixture. The explosion can only be brought about by contact of flame with the mixture. In order to avoid the contact, the flame of the safety-lamp is surrounded by wire gauze, as shown in Fig. 11. When a lamp of this kind is brought into an explosive mixture of marsh-gas and air, the mixture passes through the wire gauze and comes in contact with the flame, and a

small explosion or a series of small explosions inside the gauze occurs, but the flame of the burning gas inside the wire gauze cannot pass through and raise the temperature of the gas outside to the burning temperature. Hence no serious explosion can take place. The flickering of the flame of the lamp, and the occurrence of small explosions inside, furnish the miner with the information that he is in a dangerous atmosphere. While the safety-lamp does undoubtedly afford much protection, still explosions occur. These have been shown to be caused by the presence of coal-dust in the mines, and by the commotion of the air produced in blasting. By the aid of the coal-dust, and by sudden and violent movements of the air, it is possible for a flame surrounded by wire gauze to explode a mixture of marsh-gas and air on the other side of the gauze.

**Structure of Flames.**—The hydrogen flame consists of a thin envelope of burning hydrogen enclosing unburned gas, and surrounded by water vapor, which is the product of the combustion. The structure of other flames depends upon the complexity of the gases burned, and the conditions under which the burning takes place. In general, a flame consists of an outer envelope of gas combining with oxygen, and hence hot, and an inner part which contains unburned gas, which is comparatively cool. A part of the unburned gas is, however, quite hot, and it would combine with oxygen were it not for the fact that it is surrounded by an envelope which prevents access of air. The *outer hot part* of the flame is called the *oxidizing flame,* because it presents conditions favorable to the oxidation of substances introduced into it. The *inner hot part* is called the *reducing flame,* because it consists of highly heated substances which have the power to combine with oxygen; and hence many compounds containing oxygen lose it, or are reduced, when introduced into this part of the flame. The hottest part of the flame is about half-way between the bottom and the top. Here oxidation is taking place most energetically. The hottest part of the unburned gases is at the tip of the dark central part of the flame.

In the flame of a Bunsen burner the two parts can be easily distinguished. The dark central part of the flame extends for some distance above the outlet of the burner. If the holes at the base of the burner are partly closed, the tip of the central part of the flame becomes luminous. This luminous tip is most efficient for the purpose of reduction. The principal parts of the flame are those marked in Fig. 12. The part marked $b$ is the central cone of unburned gases; that marked $c$ is the luminous tip, the best part of the flame for reduction. $A$ is the envelope of burning gas. The hottest part of the flame is at $a$; that which is most efficient in causing oxidation is at $d$. This is further surrounded by a non-luminous envelope consisting of the products of combustion, carbon dioxide and water vapor. Certain metals placed in the upper end of the flame take up oxygen, because they are highly heated in the presence of oxygen. Certain oxides lose their oxygen when placed in the tip of the central cone, because the gases are here heated to the temperature at which they have the power to combine with oxygen.

**Blow-pipe.**—The oxidizing and reducing flames are frequently utilized in the laboratory. For the purpose of increasing their efficiency a *blow-pipe* is used. This is simply a tube with a convenient mouth-piece and a nozzle with a small opening through which air is blown into a flame by means of the mouth. The blow-pipe may be used with the flame of a candle, an alcohol-lamp, or a gas-lamp. It is commonly used with a gas-lamp. By regulating the current of air and slightly changing the position of the tip of the blow-pipe a good oxidizing flame or a good reducing flame can be produced. Some oxides are very easily reduced when heated in the reducing blow-pipe flame. Others are not. We can frequently judge of the composition of a substance by heating in the blow-pipe flame, and noticing its conduct. Some metals are easily oxidized in the oxidizing flame.



FIG. 12.

Some form characteristic films, or thin layers of oxides, on the substance upon which they are heated, which is usually charcoal; and, in some cases, it is possible to detect the presence of certain substances by the color of the film of oxide. The blow-pipe is therefore of much value as affording a method for the detection of the presence of certain elements in mixtures or compounds of unknown composition. The chemical principles involved in its use will be clear from what has already been said.

**Causes of the Luminosity of Flames.**—It is evident from what we have seen that flames differ greatly in their light-giving power. The hydrogen flame, for example, though extremely hot, gives practically no light. This is also the case with the flame of the Bunsen burner; while, on the other hand, the flame of coal-gas, burning under ordinary circumstances, and that of a candle, etc., give light. To what is the difference due? This subject has been studied very thoroughly, and it has been found that there are several causes which operate to make a flame give light, and *vice versa*. In the first place, if a solid substance which does not burn is introduced into a non-luminous flame, a part of the heat appears as light. This is seen when a spiral of platinum wire is introduced into a hydrogen flame. It is also seen when a piece of lime is introduced into the hot non-luminous flame of the oxyhydrogen blow-pipe. A similar cause operates in ordinary gas-flames to make them luminous. There are always present particles of unburned carbon, as can be shown by putting a piece of porcelain or any solid substance into the flame, when there will be deposited on it a layer of soot, which consists mainly of finely divided carbon. In the flame such particles are heated up to incandescence, or to the temperature at which they give light. Again, it has been found that a candle gives more light at the level of the sea than it does when at the top of a high mountain, as Mount Blanc, on which the experiment was actually performed. This is partly due to a difference in the density of the gases. Naturally, the denser the gas the more active the com-

bustion, the greater the heat, and the brighter the light. This last statement ceases to be true when the oxidation becomes sufficient to burn up all the solid particles in the flame. If gases, which in burning give light, are cooled down before they are burned, the luminosity is diminished, and, conversely, non-luminous flames may be rendered luminous by heating the gases before burning them. Gases which otherwise give luminous flames give non-luminous flames when diluted to a sufficient extent with neutral gases, such as nitrogen and carbon dioxide, which neither burn nor support combustion.

**Bunsen Burner.**—All the statements made in regard to the causes of the luminosity of flames are based upon carefully performed experiments. These experiments, however, cannot, for the most part, be readily repeated by the student in the laboratory in a satisfactory way. One constant reminder of the possibility of rendering a luminous flame non-luminous, and *vice versa*, is furnished by the burner universally used in chemical laboratories, and called, after the name of the inventor, the *Bunsen burner*. The construction of this burner is easily understood. It consists of a base and an upper tube. The base is connected by means of a rubber tube with the gas supply. The gas escapes from a small opening in the base, and passes upward through the tube. At the lower part of the tube there are two holes, which may be opened or closed by turning a ring with two corresponding holes in it. When the gas is turned on, it is lighted at the top of the tube. Air is at the same time drawn through the holes at the base. The result is that the flame is practically non-luminous. If the ring at the base is turned so that the air-holes are closed, the flame becomes luminous. The advantage of the non-luminous flame for laboratory use consists in the fact that it does not deposit soot, and, at the same time, it is hot.

The non-luminosity of the flame of the Bunsen burner appears to be due to several causes: (1) Dilution of the gases by means of the nitrogen of the air; (2) Cooling of the gases by the entrance of the air; (3) Burning of

the solid particles by the aid of the oxygen of the air admitted to the interior of the flame.

## COMPOUNDS OF CARBON WITH NITROGEN AND WITH SULPHUR.

**Cyanogen, $C_2N_2$.**—Carbon does not combine with nitrogen under ordinary circumstances. If, however, they are brought together at very high temperatures in the presence of metals, they combine to form compounds known as *cyanides*. Thus, when nitrogen is passed over a highly heated mixture of carbon and potassium carbonate, potassium cyanide, KCN, is formed. Carbon containing nitrogen, as animal charcoal, when ignited with potassium carbonate, reduces the carbonate, forming potassium, in presence of which carbon and nitrogen combine, forming potassium cyanide. When refuse animal substances, such as blood, horns, claws, hair, etc., are heated together with potassium carbonate and iron, a substance known as *potassium ferro-cyanide*, or *yellow prussiate of potash*, $K_4Fe(CN)_6 + 3H_2O$, is formed. When this is simply heated it is decomposed, yielding potassium cyanide:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

It is an easy matter to make the mercury salt, $Hg(CN)_2$, from the potassium salt. By heating mercuric cyanide it breaks up, yielding metallic mercury and cyanogen gas:

$$Hg(CN)_2 = Hg + C_2N_2,$$

just as mercuric oxide yields mercury and oxygen when heated:

$$HgO = Hg + O.$$

Cyanogen (from κύανος, *blue*) owes its name to the fact that several of its compounds have a blue color. It is a colorless gas, which is easily soluble in water and alco-

hol, and is *extremely poisonous.* It burns with a purple-colored flame. In aqueous solution cyanogen soon undergoes change, and a brown amorphous substance is deposited. In the solution are found hydrocyanic acid, oxalic acid, ammonia, and carbon dioxide. The principal cause of this decomposition is apparently the tendency of the nitrogen to combine with hydrogen to form the stable compound ammonia, and of carbon to combine with hydrogen and oxygen to form stable compounds like oxalic acid and carbon dioxide. One of the chief decompositions which cyanogen undergoes with water is that represented in the equation

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4H_2O = \begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} + 2NH_3.$$

The compound $\begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix}$ or $H_2C_2O_4$ is oxalic acid. This kind of decomposition with water is characteristic of cyanogen compounds. It consists, as will be seen, in the union of the nitrogen with hydrogen to form ammonia, and the union of the carbon with oxygen and hydroxyl.

**Hydrocyanic Acid, Prussic Acid, HCN.**—This acid, which is commonly known by the name prussic acid, occurs in nature in amygdalin, in combination with other substances, in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by decomposing metallic cyanides with hydrochloric acid. It is volatile and passes over. The action is represented thus:

$$KCN + HCl = KCl + HCN.$$

It can also be made by treating chloroform with ammonia:

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

Of course, the hydrochloric acid and the hydrocyanic acid formed combine with ammonia, so that the complete action is represented by this equation:

$$CHCl_3 + 5NH_3 = NH_4CN + 3NH_4Cl.$$

The product $NH_4CN$ is ammonium cyanide.

Hydrocyanic acid is a volatile liquid, boiling at 26°.1, and solidifying at − 14°. It has a very characteristic odor suggestive of bitter almonds. *It is extremely poisonous.* It dissolves in water in all proportions, and it is such a solution which is known as prussic acid. Pure hydrocyanic acid is very unstable. By standing, a brown substance is deposited from its solution. By boiling with alkalies or acids it is converted into formic acid and ammonia. This is another example of the tendency of cyanogen compounds to decompose in the presence of water, yielding ammonia and oxygen compounds of carbon. The decomposition of hydrocyanic acid takes place as represented in the equation

$$C \begin{cases} N \\ H \end{cases} + \begin{matrix} HHO \\ HHO \end{matrix} = C \begin{cases} O \\ OH \\ H \end{cases} + NH_3.$$

The relations between chloroform, formic acid, and hydrocyanic acid are instructive. By replacing all the chlorine atoms of chloroform by hydroxyl a compound of the formula $C \begin{cases} OH \\ OH \\ OH \\ H \end{cases}$ would be formed ; but this would break down by loss of water, yielding formic acid, $C \begin{cases} O \\ OH \\ H \end{cases}$.

By replacing the three chlorine atoms by one nitrogen atom hydrocyanic acid is formed ; and this in turn when decomposed in presence of water yields formic acid. These relations will be made clear by the aid of the following formulas and equations :

$$C \begin{cases} Cl \\ Cl \\ Cl \\ H \end{cases} + \begin{matrix} HOH \\ HOH \\ HOH \end{matrix} = C \begin{cases} OH \\ OH \\ OH \\ H \end{cases} + 3HCl ;$$

$$C \begin{cases} OH \\ OH \\ OH \\ H \end{cases} = C \begin{cases} O \\ OH \\ H \end{cases} + H_2O ;$$

$$C \begin{cases} Cl \\ Cl \\ Cl \\ H \end{cases} + \left. \begin{matrix} H \\ H \\ H \end{matrix} \right\} N = C \left\{ \begin{matrix} N \\ H \end{matrix} \right. + 3HCl;$$

$$C \left\{ \begin{matrix} N \\ H \end{matrix} \right. + \begin{matrix} HHO \\ HHO \end{matrix} = C \begin{cases} O \\ OH \\ H \end{cases} + NH_3.$$

**Cyanic Acid, HCNO.**—By gentle oxidation of a cyanide it is converted into a cyanate. Thus, by melting together potassium cyanide and lead oxide, potassium cyanate is formed :

$$KCN + PbO = KCNO + Pb.$$

Cyanic acid is a volatile, acrid, unstable liquid. It breaks down at once into carbon dioxide and ammonia in presence of water :

$$CONH + H_2O = NH_3 + CO_2.$$

The potassium salt is easily soluble in water, but is decomposed by it, yielding ammonia and acid potassium carbonate :

$$CONK + 2H_2O = KHCO_3 + NH_3.$$

These decompositions of cyanic acid and the cyanates further exemplify the tendency of cyanogen compounds to undergo decomposition in presence of water.

**Carbon Disulphide, CS₂.**—Just as carbon combines directly with oxygen to form the dioxide, so it combines directly with sulphur to form the disulphide ; but there is a great difference in the ease with which carbon combines with the two elements. In order to effect combination with sulphur a very high temperature is necessary. The compound is prepared on the large scale by heating charcoal to a high temperature in an upright cast-iron cylinder, and adding sulphur in such a way that it enters the bottom of the cylinder. The product is passed

through a series of tubes arranged so as to secure condensation.

Carbon disulphide is a clear liquid which has a high refractive power. It boils at 46°.2. When pure it has a pleasant odor, but if kept for a time, particularly if water is present in the vessel, it undergoes slight decomposition, and products of extremely disagreeable odor are formed. It can generally be freed from these by shaking the liquid with a little mercury and then redistilling. It burns readily, forming carbon dioxide and sulphur dixoide :

$$CS_2 + 3O_2 = CO_2 + 2SO_2 .$$

In nitric oxide it burns with an intensely brilliant flame, as can be shown by filling a cylinder with the gas, adding a few drops of the disulphide, shaking and then applying a flame. A column of brilliant flame rises from the mouth of the cylinder for an instant. A lamp has been constructed in which this flame is utilized. It is of special value in photographic work.

Carbon disulphide is only very slightly soluble in water, and is decomposed by it only very slowly. The disulphide is an excellent solvent for many substances which are not soluble in water, as, for example, fats, resins, iodine, and one of the modifications of sulphur and of phosphorus. The solution of iodine in it has a beautiful violet color; and when a water solution containing a little free iodine is shaken with carbon disulphide the latter acquires a violet color and separates below the water.

When the vapors of carbon disulphide and hydrogen sulphide are passed together over heated copper, methane and cuprous sulphide are formed, as has been stated. Methane is also formed when the vapors of carbon disulphide and of water are passed over ignited iron. While the disulphide is not easily decomposed by water at the ordinary temperature, the two compounds react when

heated in a sealed tube to 150°, the products being carbon dioxide and hydrogen sulphide :

$$CS_2 + 2H_2O = CO_2 + 2H_2S.$$

Carbon disulphide finds extensive application as a solvent, and it is also used for the purpose of destroying *phylloxera*, the insect which is so destructive to grape-vines, particularly in the wine districts of France.

**Sulphocarbonic Acid, Thio-carbonic Acid, $H_2CS_3$.**—Salts of this acid are formed by dissolving carbon disulphide in concentrated solutions of the hydrosulphides. Thus, when it is dissolved in a solution of sodium hydrosulphide this reaction takes place :

$$CS_2 + 2NaSH = Na_2CS_3 + H_2S.$$

The reaction, as will be seen, is perfectly analogous to that of carbon dioxide upon a solution of sodium hydroxide :

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$

The salts of sulphocarbonic acid are easily decomposed by water if the temperature is slightly elevated, the products being the corresponding carbonates and hydrogen sulphide :

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S.$$

When a sulphocarbonate is treated with cold dilute hydrochloric acid, the free acid separates as a dark yellow oil of a very disagreeable odor. This readily undergoes decomposition into carbon disulphide and hydrogen sulphide :

$$H_2CS_3 = CS_2 + H_2S.$$

This reaction is again perfectly analogous to the decomposition of ordinary carbonic acid into carbon dioxide and water.

**Oxysulphides.**—Products intermediate between carbonic acid and sulphocarbonic acid are possible. Such,

for example, are the compounds represented by the formulas $CO \begin{cases} SH \\ SH \end{cases}$, $CS \begin{cases} OH \\ OH \end{cases}$, etc.

**Sulphocyanic Acid, HCNS.**—Just as the cyanides take up oxygen and are converted into cyanates, so also they take up sulphur and are converted into sulphocyanates :

$$KCN + S = KCNS.$$

By suspending in water a salt of the acid, the metal of which forms an insoluble sulphide with hydrogen sulphide, and passing this gas through the liquid, a solution of the acid is obtained. When the solution is boiled the acid passes over partly unchanged, though a part is decomposed by the water into carbon dioxide, carbon disulphide, and ammonia :

$$2HCNS + 2H_2O = CO_2 + CS_2 + 2NH_3.$$

The ammonium salt of sulphocyanic acid is formed by dissolving carbon disulphide in an alcoholic solution of ammonia :

$$CS_2 + 4NH_3 = (NH_4)CNS + (NH_4)_2S.$$

**Constitution of Cyanogen and its Simpler Compounds.**—The compounds of cyanogen show, in general, a remarkable similarity to the compounds of the chlorine group. The hydrogen compound is a monobasic acid and forms a series of salts, the *cyanides*, which in general are analogous to the chlorides. Comparing the cyanides with the chlorides it is clear that in the former the group (CN), or the cyanogen group, plays the same part that the atom chlorine plays in the chlorides :

$$\begin{array}{ll} H(CN) & HCl \\ K(CN) & KCl \\ Hg(CN)_2 & HgCl_2. \end{array}$$

So also cyanic acid and hypochlorous acid are analogous :

$$\begin{array}{ll} HO(CN) & HOCl. \end{array}$$

This relation suggests that which is observed between the ammonium compounds and those of potassium and sodium. The cyanogen group is evidently univalent, as it combines with one atom of hydrogen, one of potassium, etc., and there are two ways in which we can conceive the atoms carbon and nitrogen combined to form a univalent group. If the nitrogen is trivalent and the carbon quadrivalent the structure is that represented by the formula $-C\equiv N$. If, on the other hand, the nitrogen is quinquivalent and the carbon quadrivalent the structure is $C\equiv N-$. By combination of the first group with hydrogen a compound of the structure $H-C\equiv N$ would result while with the second group the structure of the hydrogen compound would be $C\equiv N-H$. In the one case the hydrogen is in combination with carbon, in the other with nitrogen. It appears probable that in ordinary hydrocyanic acid the hydrogen is in combination with carbon, the structure being $H-C\equiv N$. This is in accordance with the formation of the acid by the action of ammonia upon chloroform, which is most readily understood on the assumption that the three atoms of chlorine are replaced by an atom of nitrogen. It has not been positively determined which of the two possible structures above given the cyanogen group has in cyanic acid. In one case the acid would have the structure $N\equiv C-OH$ ; in the other it would be $C\equiv N-OH$. It may also be $O=C=NH$. There are some reasons for believing that the ordinary cyanates are derived from an acid of the structure represented by the last formula.

# CHAPTER XXII.

### ELEMENTS OF FAMILY IV, GROUP A:
### SILICON—TITANIUM—ZIRCONIUM—CERIUM—THORIUM.

**General.**—While the elements of this group in some respects exhibit resemblances to carbon and bear to it relations similar to those which the members of the chlorine group bear to fluorine, the members of the sulphur group to oxygen, and the members of the phosphorus group to nitrogen, yet between them and carbon there are some remarkable differences. All the members of the group except titanium combine with hydrogen. The compounds formed have the formulas $SiH_4$, $ZrH_2$, $CeH_2$, and $ThH_2$. The power to form homologous series which is so characteristic of carbon is entirely wanting in the other members of the group. With the members of the chlorine group they all form compounds analogous to carbon tetrachloride, examples of which are:

$$SiCl_4, \qquad TiCl_4, \qquad ZrCl_4, \qquad CeF_4, \qquad ThCl_4.$$

Compounds analogous to hexa-chlor-ethane, $C_2Cl_6$, to tetra-chlor-ethylene, $C_2Cl_4$, and to octo-chlor-propane, $C_3Cl_8$, are:

$$\begin{array}{ccc} Si_2Cl_6 & Si_2Cl_4 & Si_3Cl_8 \\ Ti_2Cl_6 & Ti_2Cl_4 & \text{------} \end{array}$$

All the elements of the group form oxygen compounds analogous to carbon dioxide. They are:

$$SiO_2, \qquad TiO_2, \qquad ZrO_2, \qquad CeO_2, \qquad ThO_2.$$

The first three are acidic, and form salts which in composition are analogous to the carbonates. These are the

silicates, titanates, and zirconates of the general formulas

$$M_2SiO_3, \qquad M_2TiO_3, \qquad M_2ZrO_3.$$

Cerium and thorium oxides are basic. These facts suggest the relations between the members of the phosphorus group. The oxides of the last two members, antimony and bismuth, are basic, although the oxide of antimony is also acidic in its conduct towards the stronger bases.

The compounds of silicon are very abundant in nature; those of the other members of the group are rare.

## SILICON, Si (At. Wt. 28.18).

**Occurrence.**—We have already seen what an exceedingly important part carbon plays in animate nature. It is interesting to note that silicon, which in some respects from a chemical point of view resembles carbon, is one of the most important constituents of the mineral or inorganic parts of the earth. It occurs chiefly in the form of the dioxide, $SiO_2$, commonly called silica, or silicon dioxide; and in combination with oxygen and several of the common metallic elements, particularly with sodium, potassium, aluminium, and calcium, in the form of the *silicates*. Next to oxygen, silicon is the most abundant element in the earth. There are extensive mountain-ranges consisting almost entirely of the dioxide, $SiO_2$, in the form known as *quartz* or *quartzite*. Other ranges are made up of silicates, which are compounds formed by the combination of silicon dioxide and bases. The clay of the valleys and river-beds also contains silicon in large quantity, while the sand found so abundantly on the deserts and at the sea-shore is largely silicon dioxide.

**Preparation.**—Silicon does not occur in nature in the free state. The oxide, $SiO_2$, which is most abundant in the form of sand, is decomposed by heating it with potassium or magnesium, and silicon is thus set free. When magnesium is used the action is violent, and besides the silicon a compound of silicon and magnesium is formed.

Silicon has also been made by heating the oxide and carbon in the electric furnace, and by decomposing the chloride with potassium:

$$SiCl_4 + 4K = Si + 4KCl.$$

The best way to make it is by heating together potassium fluosilicate, $K_2SiF_6$, sodium, and zinc:

$$K_2SiF_6 + 4Na = 4NaF + 2KF + Si.$$

At the same time the zinc melts and the silicon which separates dissolves in the molten zinc. On cooling, it is deposited from the solution in beautiful needle-shaped crystals, around which the zinc solidifies at a lower temperature. By treating the mass with hydrochloric acid the zinc is dissolved and the crystals of silicon are left behind. When obtained by reduction of the oxide or the chloride by means of potassium, it is a brown amorphous powder. If made by decomposition of potassium fluosilicate by aluminium, it is deposited from the molten aluminium in crystals somewhat resembling graphite. Just as there are three forms of carbon, the amorphous, graphite, and diamond, so there are three corresponding forms of silicon, the amorphous brown powder, the graphitoidal, and the needles. The amorphous variety is converted into crystallized silicon by continued heating at a high temperature.

Amorphous silicon acts upon hydrofluoric acid, forming silicon tetrafluoride, $SiF_4$, and setting hydrogen free:

$$Si + 4HF = SiF_4 + 2H_2.$$

In this reaction it exhibits one of the properties of a base-forming element. Towards other acids, however, it is indifferent. It is not acted upon by sulphuric acid, nor by nitric acid, nor *aqua regia*. It dissolves, however, in potassium hydroxide, forming potassium silicate, in this case acting like an acid-forming element:

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2.$$

This form of silicon also burns in the air, forming the dioxide.

Crystallized silicon, on the other hand, does not burn in oxygen at the highest temperatures. It, however, reduces carbon dioxide and decomposes carbonates at a high temperature. It is also oxidized by a melting mixture of potassium nitrate and the hydroxide or carbonate. It combines with nitrogen at a high temperature.

Both the graphitoidal and needle-formed crystals of silicon consist of regular octahedrons. Both forms have a blackish-gray color and a metallic lustre.

**Silicon Hydride, SiH₄.**—This gas is obtained mixed with hydrogen when a compound of magnesium and silicon is treated with hydrochloric acid:

$$Mg_2Si + 4HCl = SiH_4 + 2MgCl_2.$$

Thus made, it takes fire when it comes in contact with the air, and the act is accompanied by explosion. The products of its combustion are silicon dioxide and water. When pure it forms a colorless gas which does not take fire spontaneously in the air at the ordinary temperature. If it is diluted with hydrogen, or if it is heated, it does take fire. When burned in a cylinder or narrow tube, so that free access of air is not possible, amorphous silicon is deposited upon the walls of the vessel.

**Titanium, Ti (At. Wt. 47.79).**—Titanium occurs in nature as titanium dioxide, $TiO_2$, in three distinct forms, known as rutile, brookite, and anatase; in combination with iron, as titaniferous iron which contains ferrous titanate, $FeTiO_3$; and in a number of iron ores and rare minerals. The element is obtained in the free state by decomposing potassium fluotitanate, $K_2TiF_6$, with potassium, just as silicon is obtained by decomposing potassium fluosilicate, $K_2SiF_6$, with potassium or sodium. It burns when heated in the air. It acts upon water at 100°, causing the evolution of hydrogen. It is dissolved by hydrochloric acid, forming the chloride, $Ti_2Cl_6$. At a high temperature it unites directly with nitrogen as silicon does. Titanium does not form a compound with hydrogen.

**Zirconium, Zr (At. Wt. 89.72).**—The principal form in which zirconium occurs in nature is as zircon, which is a silicate of the formula $ZrSiO_4$, derived from normal silicic acid, $Si(OH)_4$, by the replacement of the four hydrogen atoms by a quadrivalent atom of zirconium. The element is obtained in the free condition by decomposing potassium fluozirconate by heating it with aluminium to a high temperature. In this way it is obtained in crystallized form, somewhat resembling antimony. It does not burn in the air. It is dissolved by hot concentrated hydrochloric acid, and when heated in a current of hydrochloric acid gas. The product is the tetrachloride, $ZrCl_4$; and the same compound is formed when chlorine acts directly upon zirconium.

**Thorium, Th. (At. Wt. 230.87).**—This element occurs principally in the mineral thorite, which is essentially a silicate of thorium, $ThSiO_4$, analogous to zircon. It is obtained free by treating the chloride with silicon or potassium. At high temperatures it burns in the air, forming thorium dioxide, $ThO_2$.

**Cerium** so much resembles the two elements lanthanum and didymium, that although it falls in the same group as silicon, and resembles the elements of this group in some respects, it seems advisable to postpone its study until lanthanum and didymium are taken up.

## Compounds of the Elements of the Silicon Group with those of the Chlorine Group.

**Silicon Tetrachloride, $SiCl_4$.**—This compound is formed when silicon is heated in a current of chlorine, and by passing a current of dry chlorine over a heated mixture of silicon dioxide and carbon. Under these latter circumstances the following reaction takes place:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Carbon acting alone upon silicon dioxide cannot reduce it, nor has chlorine acting alone the power to convert it into the chloride. When, however, carbon and chlorine

act together both reactions take place. The tetrachloride is a colorless liquid. It is decomposed by water, forming silicic acid and hydrochloric acid. The reaction probably takes place as represented in the following equation :

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

The normal acid thus formed breaks down very readily, however, forming the ordinary acid of the formula $SiO(OH)_2$ or $H_2SiO_3$, corresponding to carbonic acid, $H_2CO_3$.

**Silicon Hexachloride, $Si_2Cl_6$,** is formed when silicon tetrachloride is heated with silicon :

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

When heated to a sufficiently high temperature it is decomposed, yielding silicon and the tetrachloride :

$$2Si_2Cl_6 = 3SiCl_4 + Si.$$

Water decomposes it, forming the corresponding hydroxyl derivative, which loses water and forms the acid $Si_2O_2(OH)_2$ :

$$Si_2Cl_6 + 6H_2O = Si_2(OH)_6 + 6HCl.$$
$$Si_2(OH)_6 = Si_2O_2(OH)_2 + 2H_2O.$$

The product is a disilicic acid, in some respects analogous to disulphuric acid.

Similar compounds of silicon with bromine and iodine are known.

**Silicon Tetrafluoride, $SiF_4$.**—This is one of the most interesting of the compounds which silicon forms with the members of Family VII. It is made by treating silicon dioxide with hydrofluoric acid. This action is secured by treating a mixture of silicon dioxide (sand) and calcium fluoride (fluor-spar) with concentrated sulphuric acid, when two reactions take place :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF ;$$
$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

The tetrafluoride escapes as a colorless gas, which forms thick clouds in moist air on account of the action of water upon it.

Water decomposes the tetrafluoride, as it does the tetrachloride. The first action probably consists in the formation of normal silicic acid and hydrofluoric acid, the normal acid then breaking down by loss of water and yielding the ordinary form of silicic acid:

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF\ ;$$
$$Si(OH)_4 = SiO(OH)_2 + H_2O.$$

The silicic acid thus formed separates as a gelatinous mass. At the same time the hydrofluoric acid acts upon some of the silicon tetrafluoride, forming the compound *fluosilicic acid*, which has the formula $H_2SiF_6$:

$$SiF_4 + 2HF = H_2SiF_6.$$

The complete action may be represented in one equation, as follows:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

The fluosilicic acid remains in solution in the water, and by treating this solution with carbonates or hydroxides of the metallic elements the salts known as the fluosilicates are obtained. The solution of the acid can be concentrated to a certain extent in a platinum vessel, but it breaks down into silicon tetrafluoride and hydrofluoric acid when it becomes concentrated. If more potassium hydroxide than is required to neutralize the acid is added to the solution, decomposition ensues, with formation of silicic acid:

$$H_2SiF_6 + 6KOH = 6KF + H_2SiO_3 + 3H_2O.$$

By water alone, however, the acid is not decomposed, and the salts are fairly stable. When heated, the salts give off silicon tetrafluoride, and fluorides are left behind:

$$K_2SiF_6 = 2KF + SiF_4.$$

**Constitution of Fluosilicic Acid.**—Attention has already been called to the fact that fluosilicic acid and silicic acid seem to be analogous substances, and that the former may be regarded as derived from the latter by the substitution of six fluorine atoms for the three oxygen atoms. According to this, fluorine has a valence higher than one, and this accords with the fact that at the ordinary temperature the density of hydrofluoric acid is greater than that required by the formula, $HF$. Assuming, then, that fluorine may act as a bivalent or a trivalent element, and for the present purpose it is immaterial which view is taken, the relation between silicic acid and fluosilicic acid is shown by the following formulas:

$$O=Si<{O-H \atop O-H} \; ; \quad F_2=Si<{F-F-H \atop F-F-H} \quad or \quad F_2=Si<{F=F-H \atop F=F-H} \cdot$$

Silicic acid         Fluosilicic acid

It is commonly held that the acid is a " double compound " made by the union of one molecule of silicon tetrafluoride with two molecules of hydrofluoric acid, and represented by the formula $SiF_4.2HF$. This is not even an attempt at an explanation of the fact that the composition of the acid is so similar to that of silicic acid. The above explanation is, however, in accordance with the composition of a large number of similar " double compounds," in which not only fluorine, but chlorine, bromine, and iodine enter.

**Titanium Tetrachloride, TiCl₄,** is formed by the direct action of chlorine on titanium, and also by passing dry chlorine over a mixture of carbon and titanium dioxide. It is, like silicon tetrachloride, a liquid. It forms crystallized compounds with water. When heated with water it is decomposed, yielding titanium dioxide and hydrochloric acid:

$$TiCl_4 + 2H_2O = TiO_2 + 4HCl.$$

Titanium also forms with chlorine the compounds $Ti_2Cl_6$ and $Ti_2Cl_4$.

**Titanium Tetrafluoride, TiF₄,** is formed in the same way as silicon tetrafluoride, by treating a mixture of titanium dioxide and fluor-spar with concentrated sulphuric acid, and by dissolving titanium dioxide in hydrofluoric acid. When treated with water it forms a compound analogous to fluosilicic acid, called *fluotitanic acid*, $H_2TiF_6$, which yields well characterized salts, the *fluotitanates*.

**Zirconium Tetrachloride, ZrCl₄,** is not completely decomposed by water, only half the chlorine being replaced by oxygen, forming a product, *zirconium oxychloride*, $ZrOCl_2$:

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl.$$

This is in accordance with the fact that zirconium acts as a base-forming as well as an acid-forming element. The chlorides of silicon and titanium are completely decomposed by water, as they are acid-forming.

The *tetrafluoride* of zirconium is obtained from zircon or zirconium silicate by mixing the finely powdered mineral with fluor-spar and passing hydrochloric acid gas over it at a high temperature:

$$ZrSiO_4 + 2CaF_2 + 2HCl = CaCl_2 + CaSiO_3 + ZrF_4 + H_2O.$$

With metallic fluorides the tetrafluoride forms salts of *fluozirconic acid*, $H_2ZrF_6$, analogous to fluosilicic and fluotitanic acids.

**Thorium Tetrachloride, ThCl₄,** is not decomposed by water at the ordinary temperature, but if its solution is evaporated to dryness hydrochloric acid is given off and thorium dioxide is left:

$$ThCl_4 + 2H_2O = ThO_2 + 4HCl.$$

**Thorium Tetrafluoride, ThF₄,** is easily made by treating the tetrachloride with hydrofluoric acid. With potassium fluoride it forms a salt of the formula $K_2ThF_6$, or *potassium fluothorate*. The chloride also forms a similar salt with potassium chloride, *potassium chlorthorate*, $K_2ThCl_6$.

**Comparison of the Chlorides of Family IV with those of Family V.**—In studying the chlorides formed by the members of the phosphorus group it was found that the chlorides of phosphorus are readily decomposed by water, forming the corresponding acids, and that the same is true of the chloride of arsenic; but that the trichlorides of antimony and bismuth are only partly decomposed by water, yielding oxychlorides. In the silicon group we find now similar differences between the members with low atomic weights and those with high atomic weights. The chlorides of silicon and titanium are completely decomposed by water at the ordinary temperature, while that of zirconium is only half decomposed, and that of thorium is not decomposed except at high temperature.

## Compounds of the Members of the Silicon Group with Oxygen, and with Oxygen and Hydrogen.

**Silicon Dioxide, $SiO_2$.**—This compound occurs very abundantly in nature in many different forms, both crystallized and amorphous. Quartz is a form of crystallized silicon dioxide which is found very widely distributed. It crystallizes in the hexagonal system in prisms and pyramids, the crystals sometimes attaining great size and beauty. Another form of the crystallized compound is that known as tridymite. Like quartz it crystallizes in the hexagonal system, but the characteristic forms are not the same as those of quartz. Further, it nearly always occurs in triplet crystals. The finer crystals of quartz are generally called *rock-crystal;* the crystalline variety in which the crystals are not well developed is called *quartzite.* The amorphous varieties of silicon dioxide frequently contain water in combination, or, rather, they are hydroxides of silicon. Examples of these forms are opal, agate, amethyst, carnelian, flint, sand, chalcedony. Some of these are colored by small quantities of other substances contained in them. Carnelian owes its color to a compound of iron, probably ferric oxide; flint contains small quantities of organic matter. The

specific gravity of the crystallized varieties is higher than that of the amorphous varieties, and there are also some chemical differences between them which will be referred to below.

Pure silicon dioxide can be made by melting sand or a finely powdered silicate with sodium carbonate, when sodium silicate is formed. This is soluble in water, and when hydrochloric acid is added to the solution silicic acid separates in the form of a gelatinous mass. By evaporating the mass to complete dryness, moistening with concentrated hydrochloric acid, and after a time treating with water, everything dissolves except silicon dioxide, which is perfectly pure and in a very finely divided state. It can also be obtained pure by passing silicon tetrafluoride into water. As we have seen, a form of silicic acid separates under these circumstances. This, when filtered, dried, and ignited, yields perfectly pure silicon dioxide.

**Properties.**—Silicon dioxide is insoluble in water and in most acids. It dissolves, however, in hydrofluoric acid, forming the tetrafluoride. It requires the temperature produced by the oxyhydrogen blow-pipe to melt it. The amorphous varieties are more easily acted upon by other substances than the crystallized. Thus, hydrofluoric acid acts much more readily upon them. When the amorphous compound is boiled with solutions of potassium or sodium hydroxide, or of the carbonates of these metals, it dissolves, forming the corresponding silicate:

$$K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2;$$
$$2KOH + SiO_2 = K_2SiO_3 + H_2O.$$

The crystallized varieties are not dissolved in this way. All forms of the dioxide act upon melting hydroxides or carbonates of potassium or sodium, and form the corresponding silicates.

**Uses.**—Plants take up silicon dioxide from the soil, and this being deposited in various part of their tissues, gives them the necessary firmness. Straw, for example,

is rich in silicon dioxide. Horse-tail, a plant of the genus *Equisetum*, is so rich in finely divided silicon dioxide that it is used for polishing. There are great natural deposits of finely divided silicon dioxide known as *infusorial earth*. This consists of the remains of diatoms. And finally silicon dioxide is found in the hair, in feathers, and in egg albumen. Silicon dioxide finds extensive application in the manufacture of mortar, glass, and porcelain. Ordinary glass, as we shall see, is a silicate of calcium and potassium or sodium, which is made by melting together sand and the carbonates of the metals mentioned.

**Silicic Acid.**—There are many varieties of silicic acid, all of which can, however, be referred to the *normal acid*, $Si(OH)_4$. This normal acid is not known in the free state in pure condition, but it is probably contained in the gelatinous precipitate which is formed when silicon tetrachloride or tetrafluoride is decomposed by water:

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

This cannot, however, be isolated, as, even by standing, it loses a molecule of water, and passes into the form $H_2SiO_3$:

$$Si(OH)_4 = OSi(OH)_2 + H_2O.$$

This is the form from which most of the ordinary silicates are derived. It cannot be isolated in pure condition, for when filtered off and exposed to the air it loses more water, and when heated to a sufficiently high temperature it is converted into silicon dioxide.

$$OSi(OH)_2 = SiO_2 + H_2O.$$

When potassium or sodium silicate in solution is treated with hydrochloric acid, most of the silicic acid separates in the form of a gelatinous mass if the solution is concentrated. If, however, the solution is dilute, a considerable part of the acid remains in solution. Further, if a concentrated solution of the silicate of potassium or

sodium is poured quickly into hydrochloric acid, or if the acid is poured quickly into the solution of the silicate, the silicic acid remains in solution. If, however, the solutions are brought together drop by drop the silicic acid separates. From these solutions of silicic acid ammonia or ammonium carbonate throws down the acid.

A solution of pure silicic acid can be obtained by means of *dialysis*. It has been found that solutions of different substances pass with different degrees of ease through porous membranes, just as gases differ as regards the ease with which they pass through porous diaphragms. This fact concerning gases was referred to in connection with hydrogen. Now, while some solutions pass readily through parchment paper, others pass through with difficulty, and some do not pass through at all. A *dialyser*, or an apparatus used in dialysis, may be made by tying a piece of parchment paper over the mouth of a ring-formed glass or rubber vessel, and placing this in another shallow vessel. Pure water is put in the outer vessel, and the solution for dialysis in the inner one. The arrangement is illustrated in Fig. 13.
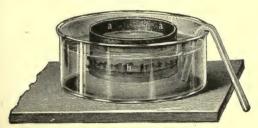


FIG. 13.

In the figure $aa$ is the hoop of gutta-percha, and $b$ is the parchment paper. When now the solution containing hydrochloric acid, sodium chloride, and silicic acid is put in the dialyser, the hydrochloric acid and sodium chloride pass readily through the membrane, while the silicic acid is left behind, and in the course of a few days, if the water in the outer vessel is renewed, the solution of silicic acid in the inner vessel will be found to be free from the other substances. This solution can be evaporated to

some extent by boiling, but when a certain concentration is reached the acid separates.   In a vacuum such a solution can be evaporated further without the formation of a deposit.   Finally, there is left a transparent mass which has approximately the composition represented by the formula $H_2SiO_3$.   The dialysed solution of silicic acid is coagulated by a very dilute solution of sodium or potassium carbonate, and by carbon dioxide itself.

When the solutions containing silicic acid are evaporated to complete dryness the acid is converted into silicon dioxide and other insoluble hydrates.   This residue is called *insoluble silicic acid*.   When this is treated with hydrochloric acid and water it remains undissolved, and if filtered off and ignited it leaves a residue of silicon dioxide.   To sum up, then : Whenever silicic acid is formed in a solution it is a more or less complex derivative of normal silicic acid, and is somewhat soluble in water, but by the processes just described the soluble acid is converted into insoluble silicic acid, as explained.

**Polysilicic Acids.**—Silicic acid is remarkable for the great number of derivatives which it yields.   Most of these bear to the normal acid relations similar to those which the various forms of phosphoric acid bear to normal phosphoric acid, and the various forms of periodic acid to normal periodic acid.   It has already been stated that salts of the acid $H_2SiO_3$ are more common than those of the normal acid.   Among the salts of the normal acid are zircon, $ZrSiO_4$, and thorite, $ThSiO_4$.   The ordinary silicates of potassium and sodium are derived from the acid $H_2SiO_3$; so also are wollastonite, $CaSiO_3$, and enstatite, $MgSiO_3$.

**Disilicic Acid** is derived from ordinary silicic acid by loss of one molecule of water from two molecules of the acid :

$$2OSi{<}^{OH}_{OH} = {OSi \atop OSi}{>}O{<}^{OH}_{OH} + H_2O.$$

Its composition is, therefore, $H_2Si_2O_5$, which may be

written $O_3Si_2(OH)_2$. Another form of disilicic acid is derived from two molecules of the normal acid by loss of one molecule of water:

$$2Si(OH)_4 = OSi_2(OH)_6 + H_2O.$$

The well-known mineral serpentine is apparently the magnesium salt of this acid. It is represented by the formula $Mg_3Si_2O_7$.

**Trisilicic Acids** are derived from three molecules of the normal acid or the ordinary acid by loss of different numbers of molecules of water. Thus, by loss of two molecules the normal acid would yield a product $H_8Si_3O_{10}$. By loss of two molecules of water this trisilicic acid would yield an acid of the formula $H_4Si_3O_8$. The structure of the first acid is expressed by formula I, and of the second by formula II, below given:

$$
\begin{array}{ccc}
Si\left\{\begin{array}{l}(OH)_3\\O\end{array}\right. & Si\left\{\begin{array}{l}OH\\O\\O\end{array}\right. & Si\left\{\begin{array}{l}OK\\O\\O\end{array}\right. \\
Si\left\{\begin{array}{l}(OH)_2\\O\end{array}\right. & Si\left\{\begin{array}{l}O\\O\end{array}\right. & Si\left\{\begin{array}{l}O\\O\end{array}\right. \\
Si\left\{(OH)_2\right. & Si\left\{(OH)_2\right. & Si\left\{O_3Al\right. \\
\textbf{I.} & \textbf{II.} & \textbf{III.}
\end{array}
$$

Orthoclase or ordinary feldspar is the aluminium-potassium salt of the second form of trisilicic acid, in which one atom of hydrogen is replaced by potassium, and three by an aluminium atom, as shown in formula III above.

**Titanium Dioxide, $TiO_2$.**—As has been stated, this is one of the principal forms in which titanium is found in nature. There are three natural crystallized varieties—rutile, brookite, and anatase. In order to prepare the pure dioxide from one of the natural forms, it is melted in finely powdered condition with potassium carbonate, when it is converted into potassium titanate, $K_2TiO_3$, the reaction being entirely analogous to that which takes place when silicon dioxide is treated in the same way:

$$K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2;$$
$$K_2CO_3 + TiO_2 = K_2TiO_3 + CO_2.$$

When titanic acid is precipitated from a solution of a titanate it appears as a hydroxide, the composition of which varies from $Ti(OH)_4$, or normal titanic acid, to $H_2Ti_2O_5$, a dititanic acid. When these substances are ignited they yield titanium dioxide. The hydroxides of titanium conduct themselves somewhat like those of silicon. They are to some extent soluble in water, and when these solutions containing sulphuric acid are much diluted and boiled, the titanium is all precipitated as a hydroxide. Titanium dioxide forms some salts with acids, among which the following are examples $Ti(SO_4)_2$ and $TiO(SO_4)$. The former is normal titanium sulphate, the latter titanyl sulphate, in which the bivalent group, TiO, or titanyl, takes the place of two hydrogen atoms.

**Zirconium Dioxide, $ZrO_2$,** is obtained by a rather complicated series of reactions from zircon. It dissolves in molten potassium or sodium carbonate, forming the corresponding zirconate, $K_2ZrO_3$. The sodium salt of normal zirconic acid, $Na_4ZrO_4$, has also been obtained.

The dioxide forms salts with acids, among which two of the sulphates are of special interest. One has the composition $ZrSO_5$, and the other $Zr_3(SO_6)_2$. The former is to be regarded as the salt of the acid $OS(OH)_4$, formed by substituting one atom of zirconium for the four atoms of hydrogen; the other is the salt of normal sulphuric acid, $S(OH)_6$, formed by substituting zirconium for all the hydrogen.

**Thorium Dioxide, $ThO_2$,** does not form thorates as the dioxides of the other members of the group. It does, however, form salts with acids. In these, thorium acts as a quadrivalent element.

**Silicides** are compounds of silicon with other elements, as, for example, with carbon. These two elements combine forming an extremely interesting compound *carbon silicide*, CSi, which is manufactured on the large scale and known in the market as *carborundum*. This is made by heating a mixture of quartz sand, coke, and common salt, or sodium chloride, in the electric furnace to 3500°, when the reaction represented below takes place:

$$SiO_2 + 2C = CSi + 2CO.$$

The product is in the main crystallized, the crystals being bluish or yellowish-green. They have the specific gravity 3.22 to 3.12. The silicide is said to be colorless when perfectly pure. It scratches ruby and chrome-steel, and on account of its hardness it is much prized as a polishing agent, being used to a considerable extent in place of emery. Pure carbon silicide is insoluble in nearly all ordinary solvents, including hydrochloric, nitric, sulphuric, and hydrofluoric acids. It is, however, decomposed by fusing caustic alkalies or their carbonates.

Many other silicides have been made, several of which are well crystallized compounds.

## FAMILY IV, GROUP B.

Allied to the members of the silicon group, yet differing from them in some important particulars, are the three elements germanium, tin, and lead. Of these the first two are more acidic in character than the last. They combine with chlorine in two proportions, forming the chlorides $GeCl_2$, $SnCl_2$, $PbCl_2$, $GeCl_4$, $SnCl_4$, $PbCl_4$. With oxygen they unite, forming the compounds $GeO_2$, $SnO_2$, and $PbO_2$. Stannic oxide, $SnO_2$, and lead peroxide, $PbO_2$, form salts with bases, and these have the composition represented by the general formulas $M_2SnO_3$ and $M_2PbO_3$, and are therefore analogous to the silicates and titanates. On the other hand, further, salts are known which are derived from the oxide $PbO$. These have the general formula $M_2PbO_2$, and are to be regarded as salts of an acid, $Pb(OH)_2$. These salts are not stable, and are not easily obtained. Most of the derivatives of lead are those in which it plays the part of a base-forming element. It will therefore be better to postpone its study until it is taken up under the general head of the base-forming elements. Notwithstanding, further, the marked analogy between some of the compounds of tin and those of the members of the silicon group, it appears on the whole advisable to treat of this element in company with lead, which it also resembles in many respects.

# CHAPTER XXIII.

## CHEMICAL ACTION.

**Retrospective.**—We have been studying the principal elements of four families and the compounds which they form with one another. No matter how simple or how complex the chemical changes studied were, certain fundamental laws governing all cases of chemical action were found to hold good. These laws have been discussed, but it will be well to recall them here before taking up other laws which are intimately connected with them. The first great law of chemical change is

I. *The law of conservation of mass.*

According to this, the amount of matter is not changed by a chemical act.

The second law is

II. *The law of definite proportions.*

According to this, the composition of every compound is always the same.

The third law is

III. *The law of multiple proportions.*

According to this, the different masses of any element which combine with a fixed mass of another or others bear simple relations to one another.

To account for the laws of definite and multiple proportions the *Atomic Theory* was proposed.

According to this, each element is made up of particles of definite weight, which are chemically indivisible, and chemical action consists in union or separation of these particles. These hypothetical particles are called *atoms.* The elements must combine in the proportion of their atomic weights or of simple multiples of these, if the atomic theory is true.

Further study showed that it is necessary to assume

the existence of larger particles than the atoms, viz., the *molecules*. According to the theory of molecules, every chemical compound and element is made up of molecules, which are the smallest particles having the same general properties as the mass. These molecules are made up of atoms which, in the case of compounds, are of different kinds, and in the case of elements, of the same kind. In the case of a few elements the atom appears to be identical with the molecule.

From the study of gases the conclusion is reached that in equal volumes of all gases under standard conditions there is always the same number of molecules (Avogadro's law). This gives us a means of determining the relative weights of molecules of gaseous substances ; and from these molecular weights it is possible to draw conclusions in regard to the atomic weights of those elements which enter into the composition of the compounds thus studied.

The formulas of chemical compounds are intended to be *molecular* formulas. They are intended to tell of what atoms and of how many atoms the molecules represented are made up.

The method of determining molecular weights based upon Avogadro's law is applicable only to gaseous substances, or to such as can be converted into gas without undergoing decomposition. While many of the compounds with which we have had to deal are of this character, many of them are not, and in regard to the molecular weights of these, we must be in doubt unless some other method applicable to liquids and solids is available. So, too, the atomic weights of those elements which enter into the composition of gaseous compounds can be deduced from the molecular weights, but plainly those which do not enter into the composition of such compounds demand some other method. For determining the atomic weights of such elements an excellent method is based upon the study of specific heats ; while for the determination of the molecular weights of solid substances which can be dissolved without decomposition a method has quite recently come into play which is based upon

the extent to which the compound raises the boiling-point or lowers the freezing-point of its solution. Both these methods will be briefly described in this chapter.

Next, it is found that there is a limit to the law of multiple proportions. While, according to this law, the masses of any element which unite with a given mass of another element bear simple relations to one another, the law is silent as to how many kinds of compounds are possible between any two elements. A careful examination of the composition of the compounds of the elements shows, however, that there is a limit to the number of atoms of one element which can combine with one atom of another element. This limit is determined by what is called the *valence* of the elements. Observations on the composition of compounds led to the hypothesis of the *linking of atoms*—the linking taking place according to the laws of valence. The arrangement of the atoms in a molecule is, according to this, the *constitution* of a compound.

Valence, as we have seen, is not a constant property of the atoms. Towards oxygen the elements which we have thus far studied have the highest valence; towards hydrogen the lowest; and, in general, towards the members of the chlorine group they exhibit an intermediate valence. The valence towards hydrogen is in most cases constant, while the valence towards oxygen and towards the members of the chlorine group varies, in some cases between comparatively wide limits, as between 1 and 7 in the chlorine group, and between 2 and 6 in the sulphur group. Further, the variations in the valence of an element generally take place from odd to odd or from even to even. In the case of chlorine it appears to vary from 1 to 3 to 5 to 7; in that of sulphur, from 2 to 4 to 6; in that of phosphorus, from 3 to 5. A knowledge of the valence of the elements is of great assistance in dealing with their compounds, as, knowing their valence, we know in general the composition of their principal compounds.

A comparison of the atomic weights finally led to the discovery that the properties of the elements are a *peri-*

*odic function of these weights.* This is the great *periodic law* of chemistry. This makes a systematic classification of the elements according to their atomic weights and their properties possible, and is full of suggestion as to the relations which the forms of matter we call elements bear to one another.

**Classification of Reactions of the Elements and Compounds Studied.**—While there is undoubtedly something confusing in the number of the compounds and their reactions which we have been studying, still, when these are interpreted in the light of the atomic theory, of the law of valence, and of the periodic law, the study is much simplified, and those things which seem to have little or no connection are found to form parts of a general system. In studying chemistry, one of the first things to be done is to learn how elements and compounds act upon one another, and what products are formed. The question of composition is one of the first which presents itself, and this must be studied before other questions can be intelligently discussed. What, then, are the most prominent facts which we have learned in studying the elements and compounds which have thus far been taken up ?

In the first place, it will have been noticed that, generally speaking, the compounds which any element forms with oxygen and hydrogen are the most prominent; that, taking the maximum oxygen compound of an element as one end of a series, the other end is formed by the hydrogen compound. These end-products in the case of chlorine, sulphur, phosphorus, and silicon are :

| Hydrogen compound. | Maximum oxygen compound. |
|---|---|
| $HCl$ | $Cl_2O_7$ |
| $H_2S$ | $SO_3(S_2O_6)$ |
| $H_3P$ | $P_2O_5$ |
| $H_4Si$ | $SiO_2(Si_2O_4)$ |

The valence towards hydrogen increases while that towards oxygen decreases regularly in the order given. With water these oxides form the acids $HClO_4$, $H_2SO_4$, $H_3PO_4$, and $H_4SiO_4$. Here the remarkable fact is ob-

served, that the number of hydrogen atoms in each of these acids is the same as that in the hydrogen compounds, and the limit of the addition of oxygen is reached in each case with four atoms of oxygen. Further, each of the first three acids appears to be related to so-called normal acids which are formed by union of the chlorine, sulphur, and phosphorus with a number of hydroxyl groups corresponding to the oxygen valence. These normal acids are

$$Cl(OH)_7, \quad S(OH)_6, \quad P(OH)_5, \quad Si(OH)_4.$$

Now, whenever a chlorine compound is subjected to oxidation under proper circumstances the final product is perchloric acid, which when isolated has probably the composition represented by the formula $HClO_4$. So when a sulphur compound is oxidized the final product is sulphuric acid, $H_2SO_4$; when a phosphorus compound is fully oxidized the final product is phosphoric acid, $H_3PO_4$; and the final product of oxidation of a silicon compound is silicic acid, $H_4SiO_4$.

By reduction of the above compounds the final products are the hydrogen compounds; but before the limit of reduction is reached intermediate products are formed. All these intermediate products are comparatively unstable, and tend to take up oxygen under ordinary circumstances and to form the stable derivative of the highest oxygen compound. Thus phosphites pass over into phosphates, sulphites into sulphates, and chlorates into perchlorates when heated. These changes are represented by the following equations:

$$2KClO_3 = KCl + KClO_4 + O_2;$$
$$4K_2SO_3 = K_2S + 3K_2SO_4;$$
$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

The highest forms are therefore evidently most stable. Turning to the compounds which the elements of Families IV, V, VI, and VII form with the members of the chlorine group, attention has repeatedly been called to the fact that

these are for the most part decomposed by water with the formation of the corresponding hydroxyl compounds.

The elements of Families IV, V, VI, and VII do not form compounds with the members of the sulphur group, nor with those of the nitrogen group, as readily as they do with hydrogen, with oxygen, and with the members of the chlorine group. Those elements which have basic character, however, like antimony and bismuth, form very characteristic compounds with sulphur. The sulphur compounds, in general, have a composition similar to that of the oxygen compounds of the same elements.

**Kinds of Chemical Reactions.**—As was pointed out in the early part of this book, all chemical reactions may be classified under three heads :

(1) Those which consist in direct combination ;

(2) Those which consist in direct decomposition ; and,

(3) Those which involve the interaction of two or more elements or compounds and the formation of two or more compounds. This is known as double decomposition or metathesis.

**Direct Combination.**—We have had to deal with a number of examples of each of these kinds of reactions. As examples of the first kind already studied the following may be mentioned :

The combination of hydrogen and chlorine to form hydrochloric acid ; the formation of ammonium chloride from ammonia and hydrochloric acid ; the formation of calcium hydroxide from calcium oxide and water ; the formation of nitrogen peroxide from nitric oxide and oxygen ; and the formation of carbon disulphide from carbon and sulphur.

As regards the combination of hydrogen and chlorine, it should be remarked that this act is the same in principle as that of metathesis. Strictly speaking, it is not a case of direct combination, as we understand it. For, as we have seen, according to the molecular theory, free chlorine and free hydrogen consist of molecules which are made up of two atoms each. Therefore, when these elements are brought together the molecules are first decomposed into atoms before the act of union can take

place. The two acts are represented by the two equations following :

$$Cl_2 + H_2 = Cl + Cl + H + H ;$$
$$Cl + Cl + H + H = 2HCl.$$

In the case also of the union of hydrochloric acid and ammonia it appears probable that a serious disarrangement of the constituent atoms is necessary in order that the act of combination may take place. According to the ammonium theory, ammonium chloride is repre-

sented by the formula $N \begin{cases} H \\ H \\ H \\ H \\ Cl \end{cases}$, which means that the

atom of chlorine and four atoms of hydrogen are in combination with the atom of nitrogen. But in order that a compound of this constitution may be formed from ammonia and hydrochloric acid, it is necessary that the molecule of hydrochloric acid should be broken down into its constituent atoms. So that this case of apparent direct combination is, as far as we can judge, in reality more complicated than it appears, and should be represented by the two equations :

$$NH_3 + HCl = NH_3 + H + Cl ;$$
$$NH_3 + H + Cl = NH_4Cl.$$

All other cases of apparent direct combination are probably of the same character, so that it is doubtful whether a single case of simple direct combination is known.

**Direct Decomposition.**—As examples of direct decomposition the following cases may be cited :

The decomposition of mercuric oxide by means of heat into mercury and oxygen ; that of ammonium chloride into ammonia and hydrochloric acid by heat ; that of potassium nitrate into potassium nitrite and oxygen

by heat; that of phosphorus pentachloride into the trichloride and chlorine by heat; that of ammonia into hydrogen and nitrogen by continued action of electric sparks; and that of nitrogen iodide by contact with a solid substance.

On close examination of each of the above cases, which are fairly typical and as simple as any that could be chosen, it will be seen that no one of them is merely a case of decomposition; for even though we must assume that the first result in each case is the setting free of the atoms of one or two elements, we must also assume that these atoms unite again to form other molecules either of elements or compounds. Thus, when mercuric oxide is decomposed we get mercury and oxygen. As far as can be determined, the mercury atoms do not unite with each other, but the oxygen atoms do, so that the total action involves decomposition and afterwards combination as represented in the equations

$$2HgO = Hg + Hg + O + O;$$
$$Hg + Hg + O + O = Hg + Hg + O_2.$$

In the case of the pentachloride of phosphorus, it is probable that the two atoms of chlorine are first given off from each molecule of the chloride, leaving a molecule of the trichloride, but the atoms of chlorine afterwards unite to form molecules as represented thus:

$$PCl_5 = PCl_3 + Cl + Cl;$$
$$PCl_3 + Cl + Cl = PCl_3 + Cl_2.$$

Similar statements hold good for all other cases of direct decomposition.

**Metathesis.**—This is the most common kind of chemical action, and indeed from what has been said in regard to direct combination and direct decomposition it will be seen that there is no essential difference between them and metathesis. Most of the reactions with which we have had to deal are examples of double decomposition

or metathesis, as : The formation of salts by the action of
bases upon acids ; the formation of the sulphides of
arsenic, antimony, and bismuth by the action of hydro-
gen sulphide upon solutions of compounds of these ele-
ments ; the setting free of hydrochloric and nitric acids
by the action of sulphuric acid upon chlorides and
nitrates ; of carbon dioxide and oxides of nitrogen by the
action of acids upon carbonates and nitrites ; and of am-
monia by treating ammonium salts with lime. Among
the more complicated examples which have been dealt
with are : The action of sulphuric acid upon potassium
iodide, giving rise to the formation of potassium sul-
phate, hydriodic acid, free iodine, sulphur dioxide, sul-
phur, and hydrogen sulphide; the action of chlorine
upon a mixture of silicon dioxide and charcoal ; the action
of silicon fluoride upon water, giving rise to the forma-
tion of silicic acid and fluosilicic acid ; and the action
of phosphorus pentachloride upon water, forming phos-
phoric and hydrochloric acids. As simple an example
of this kind of action as can be cited is that of the for-
mation of hydrogen and potassium chloride from potas-
sium and hydrochloric acid gas. The molecular weight
of potassium is not positively known, but, assuming its
molecule to be made up of two atoms, the action must be
represented in this way :

$$K_2 + 2HCl = 2KCl + H_2.$$

The next stage of complication is exhibited in the re-
action following :

$$KI + HCl = KCl + HI.$$

Examples similar to the latter, but somewhat more com-
plicated, are these :

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O ;$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl.$$

**The Cause of Chemical Reactions.**—The prime cause of
chemical reactions is something which we think of as an

attractive force exerted in different degrees between the different elements. When any elements or compounds are brought together under certain conditions the tendency is always towards the formation of the most stable compounds of those elements which can be formed under the given conditions. Thus, potassium sulphate and water are more stable forms of combination of the elements hydrogen and oxygen, and potassium, sulphur and oxygen, than sulphuric acid and potassium hydroxide are under the conditions under which the action takes place. So also the system composed of potassium chloride and hydriodic acid is more stable than that composed of potassium iodide and hydrochloric acid under the conditions of the action. Why the one system is more stable than the other we do not know, for we do not know what relations exist between the atoms in the molecules. It is convenient to think of that which causes the atoms to unite to form compounds as *chemical affinity*. It is evident that this affinity is more strongly exerted between some elements than between others. The affinity of chlorine for hydrogen is, for example, much stronger than that of chlorine for nitrogen or for oxygen. Owing, however, to the complicated character of most chemical reactions, it is extremely difficult to make measurements of the affinities of the elements, and but little progress has been made in this direction. Still, one of the great objects in view in the study of chemical phenomena is to learn as much about chemical affinity as possible.

**An Ideal Chemical Reaction.**—In every case in which two compounds act upon each other to form two new ones, several forces must be at work, as we have seen. Suppose, for example, $AB$ and $CD$ act upon each other in the gaseous condition to form two compounds $BC$ and $AD$, also both gaseous. The normal course of such a reaction would lead to the formation of not only the two compounds $BC$ and $AD$, but $AB$ and $CD$ would also be present in the resulting system. For $A$ has an affinity for $B$ as well as for $D$, and $C$ has an affinity for $D$ as well as for $B$. In the system we should have operating

the affinity of $A$ for $B$, and $A$ for $D$; of $C$ for $D$, and of $C$ for $B$. As these operate simultaneously, equilibrium is established when certain quantities of the four possible compounds are formed, the quantities depending in the first instance upon the relative strengths of the various affinities. The same remarks apply to the case in which two substances react in solution and form two products which are soluble. Here the action is not complete in any one direction, but an equilibrium is established between the four possible compounds.

**Influence of Mass.**—The proportions between the products formed in any given case is markedly influenced by the relative masses of the reacting substances. Thus, sulphuric acid acts upon potassium nitrate when the acid is in excess, forming primary potassium sulphate, $KHSO_4$, and nitric acid. On the other hand, if a large excess of nitric acid is allowed to act upon primary potassium sulphate, sulphuric acid and potassium nitrate are produced. Much attention has been given to the study of *mass action*, and the result is to show that in reactions generally this kind of action comes prominently into play. The law has been established that *chemical action is proportional to the product of the active masses of the substances taking part in the change.* It would appear from this that the decomposition of two compounds to form two new ones would not be complete, if the conditions are such that the two new compounds can act upon each other. If a large excess of one of the reacting compounds is taken, however, the reaction may be made approximately complete by reason of the mass action.

**Reactions May be Complete if one of the Products Formed is Insoluble or Volatile.**—When two substances which by interaction can form an insoluble product are brought together, the reaction generally takes place and is complete. When the substances are brought together we may imagine that, owing to interaction, a small quantity of the insoluble compound is formed at once. If this product were soluble, the action would stop before it is complete, because this new product would itself

exert its action upon the system. Being insoluble, how-
ever, it is removed from the sphere of action, and the
same reaction which caused the formation of the first
.particles of it can now be repeated, and so on, until the
reaction is complete. This is illustrated in the action of
sulphuric acid upon barium chloride in solution. The
two substances react as represented in this equation :

$$BaCl_2 + H_2SO_4 + Aq = BaSO_4 + HCl + Aq.$$

The symbol Aq is simply intended to indicate that the
reaction takes place in solution. If barium sulphate were
soluble, all four substances—barium chloride, sulphuric
acid, barium sulphate, and hydrochloric acid—would be
present in the solution after the establishment of equi-
librium. But, being insoluble, it is removed, and new
quantities are formed as long as the substances necessary
for its formation are present in the solution ; that is, until
either all the barium chloride is decomposed or all the
sulphuric acid is removed. Reactions involving the for-
mation of insoluble compounds or precipitates are among
the most common with which we have to deal, particu-
larly in the various operations of analytical chemistry.

Again, when two substances which can form a volatile
product are brought together the reaction generally takes
place and is complete. The reason why a reaction of
this kind is complete is the same as that given in the
case of the formation of an insoluble compound. Each
successive portion of the volatile product formed is re-
moved, and the reaction which gave rise to it proceeds as
long as the necessary substances are present. This kind
of action has been repeatedly illustrated. It is that, for
example, which is seen in the liberation of hydrochloric
acid from a chloride by the action of sulphuric acid ; of
carbon dioxide by the action of an acid upon a carbonate ;
and of ammonia by the action of lime upon ammonium
chloride.

An interesting example of the combined influence of
mass and the volatility of the product is seen in the action
of heated iron upon an excess of steam, and of the oxide

of iron upon an excess of hydrogen. When steam is passed over heated iron, action takes place thus :

$$4H_2O + 3Fe = Fe_3O_4 + 4H_2.$$

Hydrogen is liberated and the oxide of iron formed. When, however, hydrogen is passed over heated oxide of iron the reverse reaction takes place :

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O.$$

Owing to the excess of steam always present in the first reaction, hydrogen is constantly formed and constantly being removed. Undoubtedly the hydrogen formed acts to some extent upon the oxide, but the other reaction always takes place to a greater extent. The opposite is true when the oxide is heated in an excess of hydrogen. The principal reaction which takes place in this case is that of the hydrogen upon the oxide of iron, and the steam is carried out of the field almost as soon as formed, so that the reduction of the oxide of iron continues.

**Thermochemical Study of Affinity.**—If a mass of hydrogen and a mass of chlorine consisted of isolated atoms at rest, and, after combination, the molecules as well as their constituent atoms were at rest, then the heat evolved in the act of combination would be the result of the transformation of the potential energy of the atoms into kinetic energy, and it would be a measure of the affinity exerted between the atoms. But none of these conditions can be assumed with any confidence, and most of them undoubtedly do not exist. We have abundant evidence to show that the mass of hydrogen and that of chlorine do not consist of isolated atoms. Taking, then, the reaction between hydrogen and chlorine, it is clear, as has already been explained, that it is not simply a combination of atoms, but that the act of combination between the atoms must be preceded by the decomposition of the molecules of hydrogen and those of chlorine. The heat which is evolved in the reaction is therefore not simply the result of the combination of hydrogen and chlorine, but it is

this heat less that which is required to decompose the molecules of hydrogen and those of chlorine into atoms. The heat measured is the difference between two quantities ; and we have no means of estimating the value of these quantities. This is true of every chemical reaction. The heat evolved or absorbed in the reaction is the difference between two or more quantities, and it is not therefore a measure of affinity.

Nevertheless, some knowledge regarding the relations which the affinities of elements bear to one another can be gained by a study of the heat evolved in their reactions. Thus, the following results have been obtained in the study of chlorine, bromine, and iodine in their relations to hydrogen :

$$[H_2, Cl_2] = 2[H, Cl] - [H, H] - [Cl, Cl] = 44,000 \, c.$$
$$[H_2, Br_2] = 2[H, Br] - [H, H] - [Br, Br] = 16,880 \, c.$$
$$[H_2, I_2] \ = 2[H, I] \ - [H, H] - [I, I] \ = 12,072 \, c.$$

The meaning of these three equations will appear from an interpretation of the first. This means that when a molecule of hydrogen acts upon a molecule of chlorine to form two molecules of hydrochloric acid gas 44,000 c. of heat are evolved ; and this quantity is the difference between that which is evolved in the combination of two atoms of hydrogen with two atoms of chlorine, and that which is absorbed in the decomposition of one molecule of hydrogen into two atoms, and in the decomposition of one molecule of chlorine into two atoms. The figures thus obtained are not proportional to the affinities of chlorine, bromine, and iodine for hydrogen, but nevertheless the affinities in all probability vary in the same order.

The difficulties are much increased in more complicated cases, and it will therefore be seen that it is impossible to measure the affinity between the atoms by means of the heat evolved in reactions.

**Value of Thermochemical Measurements.**— Although the affinities of the elements for one another cannot be directly estimated by means of thermochemical measure-

ments, nevertheless these measurements are valuable, as they show a direct relation between the quantity of heat evolved and the character of the reaction which takes place in any given case. In the case above cited, for example, it is seen that the heat of formation of hydrochloric acid is greater than that of hydrobromic acid, and that of hydrobromic acid is in turn greater than that of hydriodic acid. Now, on page 94, it was stated that in general that exothermic reaction takes place which is accompanied by the greatest evolution of heat.* Accordingly, in a case in which both hydrochloric and hydrobromic acid could be produced the former would certainly be produced in larger quantity.

**Heat of Neutralization—Avidity of Acids.**—Among the measurements which have proved of value in connection with the study of the general problem of affinity, are those furnished by the heat of neutralization of acids and bases. The general method of work consisted in determining the heat evolved when equivalent quantities of different acids are neutralized by the same base and equivalent quantities of different bases are neutralized by the same acid. Knowing the heat evolved in the reactions between the various acids and bases, it is possible to determine what takes place when acids act upon salts in which decomposition is not evident, either from the formation of a precipitate or the evolution of a gas. Thus, when two molecules of nitric acid act upon one of sodium sulphate in solution, several changes are possible, as represented in the equations

(1) $Na_2SO_4 + HNO_3 = NaHSO_4 + NaNO_3;$
(2) $Na_2SO_4 + 2HNO_3 = H_2SO_4 + 2NaNO_3;$
(3) $2Na_2SO_4 + 4HNO_3 = Na_2SO_4 + 2NaNO_3 + H_2SO_4$
$$+ 2HNO_3.$$

As all the substances involved in these reactions are soluble in water, and the reactions are studied in water solution, it is clear that by ordinary methods it would be impossible to tell which of them takes place. By measuring the heat evolved, however, it has been shown

* This statement is known as Berthelot's Law of Maximum Work.

that in this and in all similar cases the base is divided between the two acids, and generally more goes to one acid than to the other. Further, it is possible to measure the division of the base between the acids, and in this way measurements of the relative strengths of acids are obtained. The figures representing the strengths of the acids measured in this way are called the *avidities of the acids.* In the case taken above as an illustration, it was found that in dilute aqueous solution two-thirds of the sodium goes to the nitric acid and one-third to the sulphuric acid. Therefore, it appears that the avidity of nitric acid is twice as great as that of sulphuric acid. Of all acids investigated, nitric and hydrochloric acids were found to have the greatest avidity. Calling this 100, the avidities of some other acids determined by this method are as given in the following table :

| Acids. | Avidity. |
|---|---|
| Nitric acid, . . . . . . . . . | 100 |
| Hydrochloric acid, . . . . . . | 100 |
| Hydrobromic acid, . . . . . . | 89 |
| Hydriodic acid, . . . . . . . . | 79 |
| Sulphuric acid, . . . . . . . . | 49 |
| Selenic acid, . . . . . . . . . | 45 |
| Hydrofluoric acid, . . . . . . . | 5 |
| Boric acid, . . . . . . . . . | 1 |
| Silicic acid, . . . . . . . . . | 0 |
| Hydrocyanic acid, . . . . . . . | 0 |

The figures given refer to equivalent quantities of the acids, i.e., quantities which can be neutralized by equal quantities of a base. Thus, 1 molecule of nitric acid, $HNO_3$, is neutralized by 1 molecule of sodium hydroxide, NaOH ; but only $\frac{1}{2}$ molecule of sulphuric acid is neutralized by 1 molecule of sodium hydroxide, and only $\frac{1}{3}$ molecule of orthophosphoric acid would be neutralized by the same quantity of base. Therefore, we say that 1 molecule of nitric acid is equivalent to $\frac{1}{2}$ molecule of sulphuric acid, and to $\frac{1}{3}$ molecule of orthophosphoric acid.

It is impossible at present to give an exact interpretation of the results above recorded, but it appears that the figures given represent the numerical relations between some common property possessed by acids, a property which we have vaguely in mind when we speak of the strength of acids. This appears more clearly when acids and bases are studied in other ways.

**Other Methods for Determining the Avidity of Acids.** —Besides the thermochemical method of studying the action of acids on bases, several other methods have been devised. Among these are the volume-chemical method, the optical method, the action of acids on insoluble salts, and the electrical method. The object in view is in all cases practically the same—to compare the influence exerted by different acids under the same circumstances, and thus to measure their avidity or, as this has also been called, their *specific coefficient of affinity*.

(1) The volume-chemical method depends upon the fact that chemical processes which take place in homogeneous liquids generally cause changes in volume. " Thus, the specific gravity of a normal caustic soda solution was found to be 1.04051, that of an equivalent solution of sulphuric acid 1.0297, that of an equivalent of nitric acid 1.03089. When equal volumes of soda solution were mixed with each of the acids, the specific gravity of the sodium sulphate solution was 1.02959, and that of the nitrate solution 1.02633. Finally, when to the solution of sodium sulphate (2 vols.) one equivalent (1 vol.) of nitric acid was added, the specific gravity became 1.02781." By means of these figures it is possible to determine to what extent the nitric acid acts upon the sulphate, and thus to draw conclusions regarding the distribution of the base between the acids. The results reached by this method agree in general with those reached by the thermochemical method.

(2) In the optical method the coefficient of refraction of various solutions is determined, and also the changes in the coefficient of refraction produced by mixing these solutions in certain ways, and thus it is possible to draw

conclusions in regard to the character of reactions which take place in solutions.

(3) An illustration of the method involving the action of acids on insoluble salts will make the method clear. A weighed quantity of calcium oxalate is treated with equivalent quantities of different acids in dilute solutions, and the quantity of the salt dissolved in a given time then determined. From the result it is possible to calculate the specific coefficients of affinity of the acids.

(4) The simplest method of all is the electrical. This consists in determining the conducting power of different substances at the same dilutions. In this way figures are obtained which bear to one another the same relations as those expressing the coefficients of affinity.

It is impossible to go into details in regard to these methods here, and it need only be said that when acids and bases are compared by the above methods, they are found to differ markedly from one another, and the order in which they are arranged by the results of the different methods is always essentially the same.

**Study of Chemical Decompositions.**—As we have seen, practically every case of chemical combination with which we have to deal is associated with the decomposition of molecules, so that it is impossible perfectly to separate the two acts of combination and decomposition. Nevertheless there are some comparatively simple cases of decomposition which have been studied with special care, and results of much importance have been obtained. The most interesting are those cases of decomposition which are included under the heads of *dissociation* and *electrolysis*. While many chemical decompositions are brought about by concussion—that is, by mechanical disturbance of the mass—the very instability of the compounds which makes these decompositions possible prevents any very profitable study of the phenomena.

**Dissociation.**—Attention has been called to the fact that many compounds, when heated to sufficiently high temperatures, are decomposed. Thus, water is partly decomposed into hydrogen and oxygen when heated to 1000°;

ammonium chloride is decomposed into ammonia and hydrochloric acid; phosphorus pentachloride, into the trichloride and chlorine; nitrogen peroxide of the formula $N_2O_4$, into the simpler compound of the formula $NO_2$, etc. Careful study of any one of these cases shows the following facts: (1) That the decomposition takes place gradually; (2) that the extent of the decomposition depends upon the temperature and pressure, and for the same compound is always the same for the same temperature and pressure; (3) that if the full amount of decomposition possible at a certain temperature is effected, and the temperature then lowered, the constituents will recombine to some extent until equilibrium at the lower temperature is established.

In a case of dissociation by heat, then, the decomposition is carried farther and farther as the temperature is raised higher and higher, and it is finally complete. On lowering the temperature again, more and more of the compound is formed by the recombination of the constitents until, when the lower temperature is again reached, there is no decomposition.

The explanation of the phenomenon of dissociation is found in the kinetic theory of gases. According to this theory, the molecules of a gas at a given temperature are moving with different velocities, though the average velocity of all the molecules is the same at the same temperature. Now, it is highly probable that the motion of the atoms within the molecules partakes of that of the molecules themselves, so that the motion of the atoms in the molecules with the greatest velocity is probably the greatest, and, in these, decomposition will take place first. When a compound gas is heated, we can easily conceive that even at a comparatively low temperature the motion of some of the molecules will be sufficient to cause their decomposition, and, as the average motion of all the molecules is constant for a given temperature, the amount of decomposition will be constant for that temperature. As the molecules are, however, moving in every direction and constantly colliding, a molecule which is decomposed at one instant

may be re-formed at the next, and one that is not decomposed may acquire motion enough to cause its decomposition. Though, as is believed, these changes are constantly taking place at every temperature, still, as has been said, the number of molecules which will be decomposed in a given mass at a given temperature and pressure will always be the same. The higher the temperature, then, the greater the number of molecules in the conditions which cause decomposition, and the smaller the number of those in the conditions favorable to formation. At each temperature and pressure an equilibrium is established, the number of molecules decomposed being equal to the number formed. It is obvious that, if one of the products of decomposition is removed, the conditions are entirely changed. Then the possibility of recombination will not exist, and total decomposition can be effected at a lower temperature than that required for total decomposition in the process of dissociation proper.

**Electrolysis.**—Some chemical compounds in solution in water conduct electricity, and at the same time they undergo decomposition. Thus, hydrochloric acid in solution in water conducts electricity and the compound is decomposed into its constituents hydrogen and chlorine, the hydrogen appearing at the negative and the chlorine at the positive pole. Compounds that act in this way are called *electrolytes*. When a current of electricity acts upon solutions of different salts, *equivalent* quantities of the metals are deposited by the same current in the same time. This is Faraday's Law. Thus if the same current were passed simultaneously through solutions of silver nitrate, $AgNO_3$, mercuric nitrate, $Hg(NO_3)_2$, cupric sulphate, $CuSO_4$, and ferric chloride $FeCl_3$, it would be found that for every 107.11 parts by weight of silver deposited there would be 99.2 parts by weight of mercury deposited, 31.56 of copper, and 18.53 of iron. These are *equivalent* quantities of these metals — quantities that take the place of one part by weight of hydrogen—and are to be distinguished from atomic quantities. Those elements which appear at

the negative pole are called *electro-positive,* and those which appear at the positive pole are called *electro-negative.* Those elements which we call *acid-forming* are electronegative, while hydrogen and the *base-forming* elements are electro-positive. The electrolysis of chemical compounds is not generally a simple decomposition into two constituents. Thus, when copper sulphate, $CuSO_4$, is decomposed, the copper is deposited at the negative pole; but no such compound as $SO_4$ appears at the positive pole. This, if formed, perhaps breaks down into oxygen and sulphur trioxide, and the latter with water would then naturally form sulphuric acid. Both oxygen and sulphuric acid as a matter of fact appear at the positive pole. The changes involved may be represented thus:

$$CuSO_4 = Cu + SO_4; \quad SO_4 = SO_3 + O; \quad SO_3 + H_2O = H_2SO_4.$$

**Electrolytic Dissociation.**—It has been known for a long time that a very weak electric current acting upon a solution of an electrolyte is sufficient to cause the ions to appear at the poles. This fact is inexplicable if it is assumed that the current is the cause of the decomposition of the electrolyte. This and some other facts which will be referred to farther on make it probable that electrolytes are at least to some extent decomposed into their constituent *ions* when they are dissolved; that these ions charged with electricity transfer their charges in the solution and thus conduct the current; and that when an ion charged with negative electricity reaches the positive pole its electricity is discharged, and the ion then ceases to be an ion and becomes an element in the free state or some compound which appears either as such or in the form of other products. According to this conception, the act of solution of an electrolyte, in water at least, involves partial breaking down or dissociation of the compound into its ions. The extent of this breaking down is determined primarily by the concentration of the solution—the greater the dilution the greater the dissociation. At infinite dilution there is complete dissociation. A water solution of hydrochloric

acid containing 36.18 grams of the acid in 1000 liters has been shown to be completely dissociated, or it is to be regarded as containing ions of hydrogen and of chlorine. These and all other ions are carefully to be distinguished from the atoms or definite compounds. An ion always carries with it a certain charge of electricity. When this is discharged the ion becomes either an element or a compound in the free state. When a solution of one electrolyte acts upon a solution of another the reaction observed is probably due to the interaction of the ions, and it is further probable that, so far as the compounds are present in the undissociated condition, they do not act upon each other. If this view is correct the reactions most familiar to us are reactions of ions, and not of elements or compounds. When, for example, an acid acts upon a base in solution it appears that, so far as they react, they are in dissociated condition. Thus hydrochloric acid and sodium hydroxide are to be regarded as acting as represented in the following equation:

$$H + Cl + Na + OH = Na + Cl + H_2O.$$

The act consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid to form water, the sodium and chlorine ions remaining as ions as in a dilute solution of sodium chloride. In the case of nitric acid and potassium hydroxide the following equation represents the reaction at infinite dilution:

$$H + NO_3 + K + OH = K + NO_3 + H_2O.$$

And so also whenever the act of neutralization takes place there is simply a union of hydrogen ions with hydroxyl ions to form water.

This conception finds strong confirmation in the fact that the heat evolved in neutralizing equivalent quantities of all acids at infinite dilution is always the same—a fact that it is difficult to explain if it is assumed that in the act of neutralization a salt is formed in the solution.

In the following table the heats of neutralization of a few acids and bases are given:

| Acid and Base. | | | | | | Heat of Neutral. |
|---|---|---|---|---|---|---|
| Hydrochloric acid and sodium hydrox., | | | | . | . | 13,700 |
| " | " | " | lithium | " | . . | 13,700 |
| " | " | " | potassium | " | . . | 13,700 |
| " | " | " | barium | " | . . | 13,800 |
| " | " | " | calcium | " | . . | 13,900 |
| Hydrobromic | " | " | sodium | " | . . | 13,700 |
| Nitric | " | " | " | " | . . | 13,700 |
| Iodic | " | " | " | " | . . | 13,700 |

As will be seen, the heat of neutralization is the same no matter what the base or what the acid may be, and as has been pointed out this fact is easily understood, if the act of neutralization consists in the union of a hydroxyl ion with a hydrogen ion to form water.

If the strength of an acid is determined by the extent to which it is dissociated, then of course those acids that are most readily dissociated are the strongest. By every method available hydrochloric and nitric acids are found to be the most readily dissociated and they are the strongest acids. The electrical method for the determination of the strength of acids is based upon this theory. The applicability of this theory to the explanation of the most common reactions that take place in solution is at present attracting the attention of chemists, and promises to be of great service to chemistry. Those reactions which are made use of for the purpose of detecting the presence of the various elements appear in fact, as has already been stated, to be reactions of the ions, and when these ions are not present the reactions are not observed. For example, when silver nitrate in solution is added to sodium chloride in solution a precipitate of silver chloride is formed, the reaction taking place as represented in this equation :

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

This reaction seems, however, to be due to the fact that ions of silver and of chlorine are present. These coming together form the insoluble molecules silver chloride which is then precipitated. There are many compounds that contain chlorine and yet do not give a precipitate

of silver chloride when treated with silver nitrate. It is believed that in these cases the compound is not ionised by the solvent in such a way as to yield ions of chlorine, and that therefore there are no chlorine ions present. An example of a compound that contains chlorine and yet does not ordinarily give the reactions of this element is potassium chlorate, $KClO_3$. A solution of this salt does not give a precipitate with silver nitrate. It is probable that the reason of this is that the salt gives, the ions K and $ClO_3$, the latter acting quite differently from the ion Cl, as we should naturally expect.

**Relations between Specific Heat and Atomic Weights.**— The fact that there is a method for the determination of atomic weights founded upon the relations existing between these weights, and the specific heat of the elements, has been mentioned. It has been found that, when equal weights of different elements are exposed to exactly the same source of heat, they require different lengths of time to become heated to the same temperature. Given exactly the same heating power, it requires 32 times as long to raise the temperature of a pound of water 10, 20, or 30 degrees as it does to raise the temperature of a pound of mercury the same number of degrees; or it takes 32 times as much heat to raise a pound of water 10, 20, or 30 degrees as it does to raise a pound of mercury the same number of degrees. Starting at the same temperature the quantity of heat required to raise the temperature of a certain weight of a substance one degree, as compared with the quantity of heat required to raise the temperature of the same weight of water one degree, is called the specific heat of the substance. Thus, from what was said above, the specific heat of mercury is $\frac{1}{32}$, or, in decimals, 0.03125. In a similar way it can be shown that the specific heat of gold is 0.03244; of zinc, 0.0955; of silver, 0.057; of copper, 0.0952.

Now, when solid elements are examined with reference to their specific heats, a very simple relation is found to exist between the numbers expressing the specific heats and the atomic weights. This relation will be made clear by a consideration of a few cases:

| Element. | Specific Heat. | Atomic Weight. |
|---|---|---|
| Silver, . . . . . | 0.0570 | 107.11 |
| Zinc, . . . . . . | 0.0955 | 64.91 |
| Cadimum, . . . . | 0.0567 | 111.10 |
| Copper, . . . . . | 0.0952 | 63.12 |
| Tin, . . . . . . | 0.0562 | 118.15 |

An examination of this table will show that the atomic weights are inversely proportional to the specific heats. We have

$$107.11 : \ 64.91 :: 0.0955 : 0.0570\,;$$
$$111.10 : \ 63.12 :: 0.0952 : 0.0567\,;$$
$$107.11 : 118.15 :: 0.0562 : 0.0570\,;\ \text{etc.}$$

These proportions are only approximately correct; but it must be remembered that the means for the determination of atomic weights and specific heats are not perfect, and in both sets of figures there are undoubtedly small errors. Hence such slight variations from absolute agreement in these proportions should occasion no surprise. The agreement is sufficiently close to indicate a close connection between the two sets of figures. This connection may be stated in another way: *The product of the atomic weight by the specific heat is a constant.* Thus, in the above cases:

$$107.11 \times 0.057 \ = 6.11\,;$$
$$64.91 \times 0.0955 = 6.20\,;$$
$$111.10 \times 0.0567 = 6.30\,;$$
$$63.12 \times 0.0952 = 6.01\,;$$
$$118.15 \times 0.0562 = 6.64.$$

From the above it appears that the quantity of heat necessary to raise masses of the elements proportional to their atomic weights the same number of degrees is the same in all cases. Suppose two elements to have the atomic weights 2 and 4. Their specific heats would be to each other as 2 to 1. That is to say, it would require twice as much heat to raise the temperature of a given mass of the element with the atomic weight 2 a

certain number of degrees, as it would require to raise the temperature of the same mass of the element with the atomic weight 4 the same number of degrees. But to raise the temperature of masses of these two elements proportional to their atomic weights would require the same quantity of heat. This fact may be stated thus:

*The atoms of all elements have the same capacity for heat.* This is only another way of stating that, to raise the temperature of an atom one degree, the same quantity of heat is always necessary.

Now, if we assume that the constant obtained by multiplying the specific heats by the atomic weights is 6.4, which is about the average of the different values found, then it is plain that, if we divide this number by the specific heat of an element, we shall obtain a number which is very near the atomic weight. If we call the atomic weight $A$, and the specific heat $H$, the following equation expresses the relation:

$$A = \frac{6.4}{H}.$$

If this law is without exceptions, it is plain that, in order to determine the atomic weight of an element, it is only necessary to determine its specific heat, and divide this into 6.4. The result will be very nearly the atomic weight. Knowing thus very nearly what the atomic weight is, it is a comparatively simple matter to determine it with great accuracy by means of chemical analysis. Unfortunately there are some marked exceptions to the law.

**Exceptions to the Law of Specific Heats.**—The elements glucinum, carbon, boron, and silicon form exceptions to the law of specific heats as this law has been stated above. At ordinary temperatures they do not follow the law. As the temperature is raised, however, the specific heat of these elements changes markedly, until finally, in the cases of carbon and silicon, a point is reached beyond which there is no marked change. Thus, at 600° the specific heat of diamond is 0.441, and at 985° it is 0.449. That of silicon is 0.201 at 185°, and 0.203 at 332°. At these

temperatures the elements obey the law. From elaborate studies which have been made on this subject, it appears that the law should be modified to read as follows :

The specific heats of the elements vary with the temperature ; but for every element there is a temperature, $T$, above which variations are very slight. The product of the atomic weight by the constant value of the specific heat is nearly a constant, lying between 5.5 and 6.5.

Notwithstanding the irregularities referred to, the law of specific heats, commonly called, from the discoverers, the law of Dulong and Petit, is of great value in the determination of atomic weights.

**Raoult's Methods for the Determination of Molecular Weights.**—One great difficulty encountered in the study of chemical compounds is the determination of the molecular weights of those which are not gases or cannot be converted into vapor by heat. From some studies on the freezing-points of solutions, it appears that quantities of compounds proportional to their molecular weights cause the same lowering of the freezing-points, provided the solvent does not act chemically upon the compound. This fact makes it possible to determine the molecular weights of substances which cannot be converted into vapor, but which can be dissolved. The application of the method is simple. Suppose water to be the solvent used. We know that this liquid solidifies or freezes at $0°$. Now, it is found that by dissolving a certain quantity of some substance in a certain quantity of water the freezing-point is lowered say .5°. Further, the quantities of other substances which are necessary to lower the freezing-point of the same quantity of water to the same extent can be determined. These quantities are proportional to the molecular weights according to the law of Raoult. If, therefore, among the substances studied there is one the molecular weight of which can be determined by the method of Avogadro, it is possible to determine the molecular weights of all of them by the method of Raoult, as will readily be seen.

So also it has been shown that quantities of compounds proportional to their molecular weights cause

the same raising of the boiling-points, provided the solvent does not act chemically upon the compounds or cause them to break down into their ions. Convenient methods have been devised for the determination of molecular weights of dissolved substances, the methods being based upon observations on the boiling-points and freezing-points. It should be noted that, when the molecular weight of a substance in solution has been determined, it does not follow that the substance has the same molecular weight when in the solid condition. This is a matter in regard to which we have practically no knowledge. It is quite possible that the molecules of solid substances may be made up of large aggregates of the simple molecules, such as probably exist in solutions or in vapors. There is, however, no method at present known that makes a determination of the complexity of these molecules, or molecular aggregates, possible.

**Determination of the Extent of Dissociation of a Dissolved Substance.**—The effect upon the boiling-point or freezing-point of a solution caused by the presence of a dissolved substance is proportional to the number of molecules in the solution or the number of individual particles, whether these are undecomposed molecules or the ions formed as a result of dissociation. Any substance that is dissociated in solution will give abnormal results if the attempt is made to determine its molecular weight by observations on the boiling-point or the freezing-point of its solutions. This method is therefore not applicable to solutions of electrolytes. On the other hand, the study of such solutions has shown that there is an increased lowering of the freezing-point for the same weight of solvent as the dilution becomes greater, a fact that points clearly to the conclusion that as the solution is diluted there is greater and greater dissociation, and advantage can be taken of this fact for the purpose of determining the extent to which dissociation has taken place in a solution of an electrolyte in water.

In general only organic compounds come within range of the methods of Raoult. These methods are now extensively used in the study of the compounds of carbon, simple forms of apparatus having been devised for this purpose. The recognition of the fact that electrolytes do not obey the simple law that holds good in the case of non-electrolytes led Arrhenius to the idea that the former are dissociated in solution—an idea which has proved of great service to the science, and is likely to revolutionize the views of chemists in regard to the action of chemical substances upon each other in solution.

# CHAPTER XXIV.

**Introductory.**—The elements thus far considered belong for the most part to the class of acid-forming elements, or those whose compounds with oxygen and hydrogen have acid properties. All the members of Family VII, Group B, are acid-forming, while the single member of Group A of the same family is both acid-forming and base-forming. All the members of Family VI, Group B, are acid-forming, while the members of Group A of this family are both acid-forming and base-forming. In Family V, Group B, there is observed a gradation of properties, the group beginning with strongly marked acid-forming elements and ending with an element, bismuth, which is more basic than acid in character. The elements of Group A, Family V, are both acid-forming and base-forming, but they have not as sharply marked characteristics as the elements of Families VI and VII. Passing now to Family IV, we found that the two most important members, carbon and silicon, belong to Group A. These two elements always act as acid-formers. A gradation of properties is observed in passing from silicon to thorium. The members of Group B of this family have the properties of the base-forming elements much more strongly marked than those of the acid-formers. There are still four families to be studied. These are families I, II, III, and VIII, the members of which are almost exclusively base-forming elements. The compounds of these elements with hydrogen and oxygen are bases, or, in other words, have the power to neutralize acids. Their oxides are for the most part basic. An exception to this is found in the case of boron, already considered, which forms a weak acid— boric acid. Its oxide is only slightly basic. The most

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strongly marked examples of base-forming elements are those which occur in Family I, Group A ; then follow in order those of Group A, Family II, and Group A, Family III. The resemblance between the members of Group B, Family I, and those of Group A of the same family is less striking than the resemblance between the two groups of any other family. Between the members of Group B, Family II, and those of Group A of the same family there is a general resemblance, while there are also differences. A similar remark applies to the relations between Groups A and B, Family III. The members of Family VIII occupy a somewhat exceptional position, as has already been pointed out. Each group of which this family consists is made up of three very similar elements with atomic weights which differ but little from one another.

**Metallic Properties.**—It has long been customary to divide the elements into two classes—the *metals* and the *non-metals.* This classification was originally based upon differences in the physical properties of the elements, the name *metal* being applied to those elements which have what is known as a metallic lustre, are opaque, and are good conductors of heat and electricity. All those elements which do not have these properties, are called *non-metals.* Gradually the name *metal* came to signify an element which has the power to replace the hydrogen of acids and form salts, and the name *non-metal* to signify an element which has not this power. This classification, as will be seen, is practically the same as that which divides the elements into acid-forming and base-forming. The latter are the metals, the former are the non-metals. The imperfection of this classification has already been commented upon, the imperfection arising from the fact that some elements belong to both classes.

**Order in which the Base-forming Elements will be Taken up.**—In studying the base-forming elements, it appears best to begin with those which have the most strongly marked character. These are the members of Family I, Group A. It further appears best to adhere as closely as possible to the arrangement in the periodic system.

Accordingly, the following order will be observed in the presentation of the elements yet to be studied :

1. Elements of Family I, Group A, or the *Potassium Group*, consisting of lithium, sodium, potassium, rubidium, and cæsium.

2. Elements of Family II, Group A, or the *Calcium Group*, consisting of glucinum, magnesium, calcium, strontium, barium, and erbium.

3. Elements of Family III, Group A, or the *Aluminium Group*, consisting of aluminium, scandium, yttrium, lanthanum, and ytterbium.

4. Elements of Family I, Group B, or the *Copper Group*, consisting of copper, silver, and gold.

5. Elements of Family II, Group B, or the *Zinc Group*, consisting of zinc, cadmium, and mercury.

6. Elements of Family III, Group B, or the *Gallium Group*, consisting of gallium, indium, and thallium.

7. Elements of Family IV, Group B, or the *Tin Group*, consisting of germanium, tin, and lead.

8. Elements of Family V, Group A, or the *Vanadium Group*, consisting of vanadium, columbium, didymium, and tantalum.

9. Elements of Family VI, Group A, or the *Chromium Group*, consisting of chromium, molybdenum, tungsten, and uranium.

10. Elements of Family VII, Group A, or the *Manganese Group*, of which manganese is the only representative.

11. Elements of Family VIII, of which there are three groups :

(A) The *Iron Group*, consisting of iron, nickel, and cobalt ;

(B) The *Palladium Group*, consisting of ruthenium, rhodium, and palladium ; and

(C) The *Platinum Group*, consisting of osmium, iridium, and platinum.

**Occurrence of the Metals.**—One of the first questions that suggests itself in connection with each element is, In what forms of combination does it occur in nature ? The chemical compounds which occur ready-formed in nature are called *minerals ;* and the minerals, and mixtures

of minerals, from which the metals are extracted for practical purposes are called *ores*. The most common ores are oxides and sulphides. Examples of these are the ores of iron, tin, copper, lead, and zinc. The carbonates also occur in large quantity in nature, and are used for the purpose of preparing some of the metals. The carbonate of zinc, for example, is a valuable ore of zinc.

**Extraction of the Metals from their Ores.**—The detailed study of the methods used in the extraction of the metals from their ores is the object of *metallurgy*. Besides the methods used on the large scale, there are others which are only used in the laboratory. The most common method of extracting metals from their ores is that used in the case of iron, which consists in heating the oxides with charcoal. If the ores used are not oxides, they must first be converted into oxides before this method is applicable. This can generally be accomplished by heating the ores in contact with the air. Under these circumstances the natural carbonates, sulphides, and hydroxides, are converted into oxides. These changes are illustrated by the following equations :

$$FeCO_3 = FeO + CO_2 ;$$
$$2FeO + O = Fe_2O_3 ;$$
$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2 ;$$
$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

A second method consists in reducing the oxide by heating it in a current of hydrogen. This has been illustrated in the action of hydrogen upon copper oxide, when the following reaction takes place :

$$CuO + H_2 = H_2O + Cu.$$

The method is efficient for many oxides, but is expensive and is not used on the large scale.

Another method of extraction consists in treating the chloride of a metal with sodium. This is illustrated in the preparation of magnesium, which is made by heating together magnesium chloride and sodium :

$$MgCl_2 + 2Na = 2NaCl + Mg.$$

Such a method is employed only in case it is impossible or extremely difficult to reduce the oxide.

Besides the above methods, there are others which will be described under the individual metals.

**The Properties of the Metals.**—As we shall find, the metals differ very markedly from one another. Some are light, floating on water, as lithium, sodium, etc.; some are extremely heavy, as lead, platinum, etc. Some combine with oxygen with great energy; others form very unstable compounds with oxygen. Some form strong bases; others form weak bases. In general, those elements which are lightest, or which have the lowest specific gravity, are the most active chemically, while those which have the highest specific gravity are the least active. Among the former are lithium, sodium, and potassium; among the latter are lead, gold, and platinum.

**Compounds of the Metals.**—The principal compounds of the metals may be conveniently classified as:

*a.* Compounds with fluorine, chlorine, bromine, and iodine; or the *fluorides, chlorides, bromides,* and *iodides.*

*b.* Compounds with oxygen, and with oxygen and hydrogen; or the *oxides* and *hydroxides.*

*c.* Compounds with sulphur, and with sulphur and hydrogen; or the *sulphides* and *hydrosulphides.*

*d.* Compounds with nitrogen; or the *nitrides.*

*e.* Compounds with carbon and with silicon; or the *carbides* and *silicides.*

*f.* Compounds with the acids of nitrogen; or the *nitrates* and *nitrites.*

*g.* Compounds with the acids of chlorine, bromine, and iodine; or the *chlorates, bromates, iodates, hypochlorites,* etc.

*h.* Compounds with the acids of sulphur, selenium, and tellurium; or the *sulphates, sulphites,* etc.

*i.* Compounds with carbonic acid; or the *carbonates.*

*j.* Compounds with the acids of phosphorus, arsenic, and antimony; or the *phosphates, arsenates,* etc.

*k.* Compounds with silicic acid; or the *silicates.*

*l.* Compounds with boric acid; or the *borates.*

It is more important to become acquainted with the general methods of preparation and the general properties

of the more important compounds than to learn details concerning many individual members of each class. Only those compounds which illustrate general principles, or which, owing to some application, happen to be of special interest, need be fully treated in this book.

The acids of which the salts are derivatives are already known to us, and in dealing with the acids frequent reference has been made to the methods of making the salts, and to some of their more important properties. It will be well, before taking up the metals systematically, briefly to treat of the general methods of preparation, and the general properties of the different classes of metallic compounds. It must be borne in mind, however, that the only way to become familiar with these substances and their relations is by working with them in the laboratory.

**Chlorides.**—The chlorides, as well as the fluorides, bromides, and iodides, may be regarded as the salts of hydrochloric, hydrofluoric, hydrobromic, and hydriodic acids, or simply as compounds of the metals with the members of the chlorine family. The most important of these compounds are the chlorides, and these well illustrate the conduct of the others.

The chlorides are made by treating a metal with chlorine, or with hydrochloric acid ; by treating an oxide or a hydroxide with hydrochloric acid ; by treating an oxide with chlorine and a reducing agent, like carbon ; by treating a salt of a volatile acid with hydrochloric acid ; by treating a salt of an insoluble acid with hydrochloric acid ; by adding hydrochloric acid or a soluble chloride to a solution containing a metal with which chlorine forms an insoluble compound ; and by adding to a solution of a chloride a salt, the acid of which forms with the metal of the chloride an insoluble salt, while the metal contained in it forms with chlorine a soluble chloride.

Only two of the above methods are peculiar to chlorides. These are the treatment of the metals with chlorine, and the treatment of oxides with chlorine and a reducing agent. The others involve principles which

are also involved in the preparation of all salts, and they may therefore be treated of in a general way.

The formation of chlorides by direct treatment of the metals with chlorine is the simplest method of all. It has been illustrated in studying chlorine. It was found that chlorine combines with other elements with great ease. Thus, iron, copper, and tin combine with it, as represented in the following equations :

$$Cu \ + Cl_2 \ = CuCl_2 \ ;$$
$$2Fe + 3Cl_2 = 2FeCl_3 \ ;$$
$$Sn \ + 2Cl_2 = SnCl_4.$$

The preparation of chlorides by treating oxides with chlorine and a reducing agent has been illustrated in the making of boron trichloride and of silicon tetra-chloride. It is used in making aluminium trichloride. For this purpose, chlorine is passed over a heated mixture of aluminium oxide and charcoal, when reaction takes place according to the following equation :

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

The interesting character of this reaction was referred to in connection with the similar preparation of the chlorides of boron and silicon. In this case, as in those, there are two reactions involved. The carbon alone cannot reduce the oxide ; nor can the chlorine alone decompose it to form the chloride. But when the carbon and chlorine act together, they assist each other, and as a consequence the oxide is transformed into the chloride.

The other methods for preparing chlorides are, as has been said, general in character and are applicable to most salts.

**Formation of Salts in General.**

1. *By treating a metal with an acid.*—This is the simplest method. It has been illustrated in the preparation of zinc sulphate by the action of zinc on sulphuric acid :

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Other common examples are those represented in the follow equations :

$$Fe + H_2SO_4 = FeSO_4 + H_2 ;$$
$$Zn + 2HCl = ZnCl_2 + H_2.$$

2. *By treating an oxide or a hydroxide with an acid.*— This is of more general application than the preceding method. As it has been studied in some detail in connection with the subject of salts (see pp. 129–133), it need not be further considered here.

3. *By treating the salt of a volatile acid with another acid.* —This method has been repeatedly illustrated in the decomposition of carbonates and nitrites by acids in general. While carbonic acid and nitrous acid themselves are perhaps not formed in these reactions, and we cannot say that the carbonates and nitrites are salts of volatile acids, yet the decomposition-products of these acids are volatile at ordinary temperatures. The decomposition of carbonates by acids has been pretty fully studied, though attention was not directed to the fact that this kind of action may be utilized for the purpose of making salts. As some carbonates occur in large quantity in nature or in the market, salts are frequently made by treating them with acids. Thus, magnesium sulphate is made by treating magnesium carbonate with sulphuric acid :

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2 ;$$

and calcium chloride is made by dissolving calcium carbonate in hydrochloric acid :

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2 ; etc.$$

4. *By treating a salt of an insoluble acid with another acid.*—This case does not occur practically, as there are no common, insoluble acids. The principle involved is illustrated to some extent by the decomposition of a soluble silicate. Sodium silicate, for example, is soluble. When its solution in water is treated with an acid

the silicic acid is partly precipitated, as we have seen

$$Na_2SiO_3 + 2HCl + H_2O = Si(OH)_4 + 2NaCl.$$

The silicic acid formed is, however, not perfectly in-soluble in water, so that the reaction is not complete. In any case the reaction is not one that is used for the preparation of salts.

5. *By the action of two salts upon each other.*—This method can be best described by means of an example. Suppose it is desired to prepare copper chloride by the action of two salts upon each other. Copper chloride is soluble. If copper sulphate and barium chloride are brought together in solution, the products are insoluble barium sulphate and soluble copper chloride :

$$CuSO_4 + BaCl_2 = BaSO_4 + CuCl_2.$$

By simply filtering off the barium sulphate, a solution of copper chloride is obtained.

6. *By precipitation.*—This method is illustrated in the formation of barium sulphate, referred to in the last paragraph. Obviously, it is applicable only to difficultly soluble or insoluble salts. Many carbonates and phosphates can be made in this way.

**General Properties of the Chlorides.**—Most of the chlorides of the metals are soluble in water without decomposition, though many of them are decomposed when heated to a sufficiently high temperature with water. It will be remembered that the chlorides of the non-metallic or acid-forming elements are decomposed by water, yielding the corresponding oxides or hydroxides. The chlorides of some elements which are partly basic and partly acid are only partly decomposed. This is illustrated by the chloride of antimony, which with water forms an oxychloride :

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

The chlorides of the most strongly marked metals, like potassium, sodium, etc., are not decomposed by water. Calcium chloride dissolves with great ease, and, if the solution is evaporated, the chloride is again obtained. If, however, the attempt is made to drive off all the water by heat, some of the chloride is converted into the oxide as represented in the equation

$$CaCl_2 + H_2O = CaO + 2HCl.$$

Magnesium chloride is completely decomposed, if its solution in water is evaporated to dryness, the action being the same in character as that which takes place in the case of calcium chloride. The chlorides of iron and aluminium and of many other metals act in the same way. Silver chloride and mercurous chloride, $HgCl$, are insoluble in water. Lead chloride is difficultly soluble in water. If, therefore, on adding hydrochloric acid or a soluble chloride to a solution, a precipitate is formed, the conclusion is generally justified that one or more of the three metals—silver, lead, or mercury—is present. By taking into account the differences between these chlorides, it is not difficult to decide of which of them a precipitate consists.

The chlorides are for the most part stable when heated, though a few lose some of their chlorine just as phosphorus pentachloride does. An example of this is presented by platinic chloride, $PtCl_4$, which when heated breaks down into platinous chloride, $PtCl_2$, and chlorine :

$$PtCl_4 = PtCl_2 + Cl_2.$$

The chlorides are for the most part decomposed when treated with sulphuric acid, as has been shown in the action of sulphuric acid upon sodium chloride. Under these circumstances hydrochloric acid is given off, and the sulphate of the metal with which the chlorine was in combination is formed. In general, the reaction is represented by such equations as the following :

$$2MCl + H_2SO_4 = M_2SO_4 + 2HCl;$$
$$MCl_2 + H_2SO_4 = MSO_4 + 2HCl; \text{ etc.}$$

Under ordinary circumstances, chlorides are not decomposed by any acid except sulphuric acid.

**The So-called Double Chlorides and Similar Compounds of Fluorine, Bromine, and Iodine.**—These compounds and their relations to the oxygen salts have been repeatedly referred to. Many chlorides combine with the chlorides of the stronger metals, like sodium and potassium, forming well-characterized compounds. Generally, these double chlorides are analogous to the oxygen salts in composition, differing from them only by containing two atoms of chlorine in the place of each of the oxygen atoms. As examples of these salts of the *chloro-acids* those which are formed by the chlorides of platinum, antimony, chromium, and gold may be mentioned. Platinic chloride, $PtCl_4$, combines with other chlorides, forming salts of the general composition expressed by the formula $PtCl_4 + 2MCl$, or $M_2PtCl_6$. Antimony chloride, combines with three molecules of potassium chloride forming the compound $SbCl_3 + 3KCl$, or $K_3SbCl_6$. Chromium chloride forms similar compounds, $K_3CrCl_6$, $Na_3CrCl_6$; and gold chloride forms compounds of the general formula $MAuCl_4$, which may be regarded as made up of one molecule of auric chloride, $AuCl_3$, and one molecule of a chloride like potassium chloride. A careful study of the double chlorides and the similar compounds of fluorine, bromine, and iodine shows that the chlorides of sodium and potassium, and of the other elements of the group to which these metals belong, combine with most other chlorides to form so-called double salts, and that *the number of molecules of potassium or sodium chloride which combine with another chloride is limited by the number of chlorine atoms contained in the other chloride.* Thus, a chloride of the formula $MCl_2$ may form the double chlorides $MCl_2.KCl$ and $MCl_2.2KCl$, but not $MCl_2.3KCl$. So, further, a chloride of the formula $MCl_3$ may form three different double chlorides with the same metallic chloride. Those with potassium will have the formulas $MCl_3.KCl$, $MCl_3.2KCl$, and

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* There are a few exceptions to this rule, but it undoubtedly holds good in by far the largest number of cases.

$MCl_3.3KCl$, but a double chloride of the formula $MCl_3.4KCl$ and more complicated cases seem to be impossible. Double fluorides are known in large numbers. Among the best-known are the fluosilicates. Aluminium forms double fluorides, one of which, having the formula $Na_3AlF_6$ or $AlF_3.3NaF$, is the well-known mineral *cryolite.* All these so-called "double salts" are easily explained by the aid of the hypothesis that the halogen contained in them has a valence greater than one, and that a double atom, like $Cl_2$, $F_2$, etc., or $-Cl-Cl-$, $-F-F-$, plays the same part that oxygen does in the oxygen salts. The following table contains the general formulas of the possible double chlorides with potassium chloride, according to the above view concerning them:

| | | | |
|---|---|---|---|
| $MCl.KCl$ | $MCl_2.KCl$ | $MCl_3.KCl$ | $MCl_4.KCl$ |
| | $MCl_2.2KCl$ | $MCl_3.2KCl$ | $MCl_4.2KCl$ |
| | | $MCl_3.3KCl$ | $MCl_4.3KCl$ |
| | | | $MCl_4.4KCl$ |

These may also be written thus:

| | | | |
|---|---|---|---|
| $KMCl_2$ | $KMCl_3$ | $KMCl_4$ | $KMCl_5$ |
| | $K_2MCl_4$ | $K_2MCl_5$ | $K_2MCl_6$ |
| | | $K_3MCl_6$ | $K_3MCl_7$ |
| | | | $K_4MCl_8$ |

**Different Chlorides of the Same Metal.**—Just as sulphur, selenium, phosphorus, and the other acid-forming elements combine with chlorine and the other members of the chlorine group in more than one proportion, so many of the metals combine with the members of the chlorine group in more than one proportion. Thus, mercury forms the two chlorides, $HgCl_2$ and $HgCl$, known respectively as mercuric and mercurous chlorides; iron forms the two chlorides $FeCl_3$ and $FeCl_2$, known as ferric and ferrous chlorides; and tin forms stannic chloride, $SnCl_4$, and stannous chloride, $SnCl_2$. The conversion of a higher chloride into a lower one is called an act of

reduction. The change can generally be effected by means of nascent hydrogen:

$$SnCl_4 + 2H = SnCl_2 + 2HCl.$$
$$FeCl_3 + H = FeCl_2 + HCl.$$

The conversion of a lower chloride into a higher one is generally spoken of as an act of oxidation, for the reason that it is most commonly effected by the action of oxygen. Thus the most convenient way to transform ferrous chloride into ferric chloride is to treat it in solution in hydrochloric acid with an oxidizing agent, when a double action takes place, as represented in the following equation:

$$2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O.$$

The same change can be effected by the direct action of chlorine:

$$FeCl_2 + Cl = FeCl_3.$$

In this case it would obviously be incorrect to speak of the process as one of oxidation.

Another method of reduction, besides that referred to above, involving the action of nascent hydrogen, is that illustrated in the equation

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4.$$

In this case mercuric chloride is changed to mercurous chloride by the action of stannous chloride. The latter unites with chlorine so readily that it extracts it from some other chlorides, and is itself transformed into stannic chloride. While, therefore, we say that the stannous chloride reduces the mercuric chloride, it is equally true to say that the mercuric chloride *chlorinates* the stannous chloride.

**Oxides.**—The oxides occur very extensively in nature, and are among the most common ores of some of the important metals. The oxides of iron, tin, and manganese, for example, occur in nature. They can be made by oxidizing the metals, by heating nitrates, carbonates, and hydroxides, and by heating some sulphides in contact with the air.

When magnesium is burned it is converted into magnesium oxide :

$$Mg + O = MgO.$$

When lead nitrate is heated it gives off oxygen and an oxide of nitrogen, and lead oxide is left behind :

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

When calcium carbonate is heated it yields calcium oxide and carbon dioxide :

$$CaCO_3 = CaO + CO_2.$$

When aluminium hydroxide, $Al(OH)_3$, is heated it loses water, and aluminium oxide is left behind :

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

The sulphide of iron, when heated in contact with the air, or " roasted," is converted into ferric oxide and sulphur dioxide.

Most of the oxides of the metals are insoluble in water. Those of Group A, Family I, are soluble, but are converted by water into the corresponding hydroxides.

The oxides are acted upon generally by acids forming the corresponding salts. If the salt with a certain acid is insoluble, the salt is not formed by the action of that acid on the oxide unless the acid or its anhydride is fusible and not volatile, when by fusing them together the salt is formed.

**Different Oxides of the Same Metal.**—Just as there are different chlorides of the same metal, so there are different oxides, and indeed there is greater variety among these than among the chlorides. Iron forms three oxides, ferric oxide, $Fe_2O_3$, ferroso-ferric oxide, $Fe_3O_4$, and ferrous oxide, $FeO$; mercury forms the two oxides $HgO$ and $Hg_2O$; etc. The lower oxides are converted into the higher by oxidation, and the higher into the lower by reduction. The higher oxides of several of the metals are acidic. This is markedly so in the case of chromium and manganese.

**Hydroxides.**—The hydroxides are formed by treating oxides with water and by decomposing salts by adding soluble hydroxides to their solutions. In general, whenever a salt is decomposed by a strong base, the base of the salt separates in the form of the hydroxide. The formation of a hydroxide by the action of water on an oxide is well illustrated by the action of water on lime or calcium oxide, a process which is familiarly known as *slaking* :

$$CaO + H_2O = Ca(OH)_2.$$

Most of the hydroxides of the metals are insoluble in water. If a soluble hydroxide is added to a solution containing a metal whose hydroxide is insoluble, the latter is precipitated. Thus, if a solution of sodium hydroxide is added to a solution of a magnesium salt, magnesium hydroxide is precipitated :

$$MgSO_4 + 2NaOH = Na_2SO_4 + Mg(OH)_2.$$

So, also, when a solution of a ferric salt is treated with sodium hydroxide, a precipitate of ferric hydroxide is formed :

$$FeCl_3 + 3NaOH = 3NaCl + Fe(OH)_3.$$

Only the hydroxides of the members of the potassium family, and some of the members of the calcium family, are soluble in water. The hydroxides of sodium and potassium are called *alkalies*. The solution of ammonia in water acts like a soluble hydroxide, and probably contains ammonium hydroxide, $NH_4(OH)$, formed by the action of water on ammonia :

$$NH_3 + H_2O = NH_4(OH).$$

Now, when any one of the soluble hydroxides is added to a salt containing any metal which does not belong to the potassium or calcium family, an insoluble compound is formed.

**Decomposition of Salts by Bases.**—The decomposition of salts by bases is analogous to the decomposition by

acids.   When a soluble base acts upon a salt, there are four possible kinds of action :

1. The base from which the salt is derived may be volatile, or may break up, yielding a volatile product.

In this case, decomposition takes place and the volatile base is given off.   This is not a common case except among the compounds of carbon.   The one illustration which we have had is the decomposition of ammonium salts by calcium hydroxide and sodium hydroxide, when the volatile compound ammonia, $NH_3$, is given off.

2. The hydroxide, or base from which the salt is derived, may be insoluble or difficultly soluble in water, and not volatile.

In this case, if both the salt and the base are in solution, decomposition takes place, and the insoluble or difficultly soluble hydroxide, or base, is precipitated. This has already been illustrated.

3. The base from which the salt is derived may be soluble and not volatile.

This is the case, for example, when sodium hydroxide is added to a solution of potassium nitrate.   Here sodium nitrate, potassium nitrate, sodium hydroxide, and potassium hydroxide may all be present in the solution, and investigation has shown that all are present and that the quantity of each depends upon the masses of the substances brought together, and upon their affinities.

4. The fourth case is that in which a soluble hydroxide forms an insoluble salt with the acid of a soluble salt, leaving a soluble hydroxide in solution.

This is illustrated by the action of calcium hydroxide on a solution of sodium carbonate, when insoluble calcium carbonate is thrown down, and sodium hydroxide remains in solution, as represented in the equation

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

Some basic hydroxides, which are precipitated by soluble hydroxides, have a weak acid character, and, after they are precipitated, they redissolve in an excess of the soluble hydroxide.   This is true, for example, of aluminium,

chromium, and lead. The salt-like compounds thus formed are generally quite unstable. The precipitation and subsequent solution of the hydroxides of the three metals named take place thus:

$$AlCl_3 \quad + 3NaOH = Al(OH)_3 \quad + 3NaCl;$$
$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O;$$
$$CrCl_3 \quad + 3NaOH = Cr(OH)_3 \quad + 3NaCl;$$
$$Cr(OH)_3 + 3NaOH = Cr(ONa)_3 + 3H_2O;$$
$$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 \quad + 2NaNO_3;$$
$$Pb(OH)_2 + 2NaOH = Pb(ONa)_2 + 2H_2O.$$

In some cases where a soluble hydroxide is added to a salt, an oxide is precipitated instead of the hydroxide. This is analogous to the formation of an anhydride of an acid instead of the acid itself, as when carbonates, sulphites, and nitrites are decomposed.

When a silver salt is treated with a soluble hydroxide, silver oxide is at once precipitated. The same is true of mercury salts:

$$2AgNO_3 + 2KOH = Ag_2O + H_2O + 2KNO_3;$$
$$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl.$$

It is probable that the first product is the hydroxide, and that this breaks down into the oxide and water:

$$2AgNO_3 + 2KOH = 2AgOH + 2KNO_3;$$
$$2AgOH = Ag_2O + H_2O;$$
$$HgCl_2 + 2NaOH = Hg(OH)_2 + 2NaCl;$$
$$Hg(OH)_2 = HgO + H_2O.$$

Some hydroxides are converted into the oxides by simply boiling the liquids in which they are suspended. Thus, when a salt of copper is treated with a soluble hydroxide, copper hydroxide is first precipitated; but if the solution in which it is suspended is boiled, it is soon changed to the oxide:

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2;$$
$$Cu(OH)_2 = CuO + H_2O.$$

The hydroxides corresponding to some of the higher oxides of the metals, as those of chromium and manganese, are acids.

The hydroxides of most of the metals are decomposed by heat into water and the corresponding oxides. Those of the alkali metals, as potassium and sodium, are not, however, decomposed by heat.

**Sulphides.**—Many sulphides are found in nature, as, for example, iron pyrites, $FeS_2$; lead sulphide, or galenite, $PbS$; copper pyrites, $FeCuS_2$; etc. They are made in the laboratory by heating metals with sulphur; by treating solutions of salts with hydrogen sulphide; by treating solutions of salts with soluble sulphides; and by reducing sulphates. Attention has been called to the fact that the sulphides are analogous in composition to the oxides, and that they are to be regarded as salts of hydrogen sulphide formed by replacing the hydrogen of the acid by metals.

The formation of sulphides by the direct combination of sulphur with the metals is shown in the formation of lead sulphide and copper sulphide:

$$Pb + S = PbS;$$
$$2Cu + S = Cu_2S.$$

The formation of sulphides by the action of hydrogen sulphide upon solutions of salts was discussed at some length under Hydrogen Sulphide (which see). The extensive use made of this reaction in chemical analysis was also referred to.

The action of soluble sulphides or solutions of salts is in general the same as that of hydrogen sulphide, but in some cases, in which the former will not act, the latter will. Thus, hydrogen sulphide will not precipitate iron sulphide from a solution of an iron salt, because iron sulphide is easily acted upon by dilute acids. Thus, when hydrogen sulphide is passed into a solution of ferrous chloride, it naturally tends to form the sulphide $FeS$:

$$FeCl_2 + H_2S = FeS + 2HCl.$$

But ferrous sulphide, FeS, is acted upon by dilute hy‧drochloric acid, and is converted by it into ferrous chloride and hydrogen sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S.$$

It is therefore obvious that the first reaction cannot take place.

If, however, a soluble sulphide, as sodium or ammonium sulphide, is added to a solution of an iron salt, iron sulphide is precipitated, as in this case no free acid is formed. Thus, when ferrous chloride and ammonium sulphide are brought together the reaction takes place as represented in the equation

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

In ammonium chloride the ferrous sulphide is not soluble.

The formation of a sulphide by reduction of a sulphate is illustrated by the formation of barium sulphide by heating a mixture of barium sulphate and charcoal:

$$BaSO_4 + 4C = BaS + 4CO;$$

and by the formation of copper sulphide by heating copper sulphate in a current of hydrogen:

$$CuSO_4 + 4H_2 = CuS + 4H_2O.$$

The sulphides of the alkali metals are soluble in water. Those of the other metals are insoluble. It should be remarked, however, that aluminium and chromium do not form sulphides, or, at least, if they do, the compounds are decomposed by water into hydroxides and hydrogen sulphide. Barium sulphide is decomposed by water, and probably magnesium sulphide also.

The sulphides are stable when heated without access of air; but if heated in the air they are converted into oxides of the metals and sulphur dioxide, or, in some cases, they take up oxygen and are converted into sulphates. The conversion of sulphides into oxides and sulphur dioxide by heating in contact with the air has

been repeatedly referred to. The process is carried on on the large scale in the preparation of iron ores for reduction, and is called *roasting.* The conversion of a sulphide into a sulphate by heating is a simple process of oxidation. Copper sulphide is converted into the sulphate when heated for some time :

$$CuS + 4O = CuSO_4.$$

This is the reverse of the reaction mentioned by which a sulphate is converted into a sulphide by reduction.

Some sulphides, as those of sodium, potassium, and ammonium, take up sulphur in much the same way that they take up oxygen, and form the polysulphides. The two reactions appear to be entirely analogous :

$$K_2S + 4O = K_2SO_4 ;$$
$$K_2S + 4S = K_2SS_4, \text{ or } K_2S_5.$$

**Hydrosulphides.**—The hydrosulphides bear the same relation to the sulphides that the hydroxides bear to the oxides. They are not, however, as numerous nor as easily obtained as the hydroxides. When a hydrosulphide, as, for example, potassium hydrosulphide, KSH, is added to a salt containing a metal whose sulphide is insoluble, the sulphide, and not the hydrosulphide, is precipitated. Thus, copper sulphate and potassium hydrosulphide give copper sulphide :

$$CuSO_4 + 2KSH = CuS + H_2S + K_2SO_4.$$

If the reaction took place in the same way that it does with the hydroxide, the product would be copper hydrosulphide :

$$CuSO_4 + 2KSH = Cu(SH)_2 + K_2SO_4.$$

If this is formed it certainly breaks down into copper sulphide and hydrogen sulphide, in the same way that copper hydroxide breaks down into copper oxide and water, only more easily :

$$Cu(SH)_2 = CuS + H_2S ;$$
$$Cu(OH)_2 = CuO + H_2O.$$

The only hydrosulphides known are derived from the members of the potassium and calcium groups, and these are soluble. They are formed by saturating solutions of the corresponding hydroxides with hydrogen sulphide. Potassium hydrosulphide is formed thus:

$$KOH + H_2S = KSH + H_2O.$$

Ammonium hydrosulphide is formed thus:

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

It also appears probable that whenever a sulphide is dissolved in water it is converted into a hydrosulphide and a hydroxide. Thus it seems to be true that potassium sulphide is converted into the hydrosulphide and hydroxide:

$$K_2S + H_2O = KSH + KOH.$$

**Sulpho-salts.**—The relation of the sulpho-salts to the sulphides has already been explained. It is like that of the ordinary oxygen salts to the oxides, and that of the chloro-salts, or double chlorides, to the chlorides. They are formed by dissolving the sulphides of certain metals, particularly tin, arsenic, and antimony, in the sulphides of the members of the potassium group:

$$As_2S_3 + 3K_2S = 2K_3AsS_3;$$
$$As_2S_5 + 3K_2S = 2K_3AsS_4;$$
$$SnS_2 + K_2S = K_2SnS_3, \text{ etc.}$$

These sulpho-salts are decomposed by the ordinary acids, the insoluble sulphides being precipitated thus:

$$2K_3AsS_3 + 6HCl = As_2S_3 + 6KCl + 3H_2S;$$
$$2K_3AsS_4 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

**Nitrates.**—The nitrates are formed by dissolving the metals in nitric acid, and by treating oxides, hydroxides, carbonates, and some other easily decomposed salts with nitric acid. The action of nitric acid upon metals was discussed under the head of Nitric Acid (which see). It was pointed out that the acid gives up a part of its

oxygen to the metal and forms different oxides, accord-ing to the conditions. Thus, when the acid acts upon copper the main product of the reduction is nitric oxide, but by changing the concentration of the acid a considerable quantity of nitrous oxide is formed. When zinc is dissolved in nitric acid a part of the acid is reduced to ammonia.

The nitrates are soluble in water, and all are decom-posed by heat. Some of them when heated lose only a third of their oxygen and are reduced to nitrites. This is true of potassium nitrate, the decomposition of which is represented by the equation

$$KNO_3 = KNO_2 + O.$$

Most of the nitrates, however, are decomposed further, forming oxides. This has been shown in the case of lead nitrate, which when heated is converted into lead oxide, while nitrogen peroxide and oxygen are given off:

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

If the oxide of the metal is decomposed by heat, as in the case of mercury, of course the product will be the metal.

**Chlorates.**—These salts, except potassium chlorate, are not commonly met with. Potassium chlorate is manu-factured in large quantity, and the other chlorates are generally made from it. The chlorates are soluble in water, and are decomposed by heat more easily than the nitrates are. They are first converted into perchlorates, and these are further decomposed by higher heat into chlorides and oxygen.

The *hypochlorites* are formed by treating some of the metallic hydroxides in dilute solution with chlorine. This has been illustrated in the formation of "bleaching powder," which contains calcium hypochlorite or a com-pound closely related to it. The hypochlorites, like the chlorates, are decomposed by heat.

**Sulphates.**—The general relations of the sulphates to sulphuric acid were treated of under Sulphuric Acid (which see). Some of these salts occur in nature in large

quantity, as those of calcium and barium. The former is known as *gypsum*, the latter as *heavy spar*. Sulphates are made by treating metals, metallic hydroxides or oxides, carbonates, etc., with sulphuric acid ; and by treating a solution containing a metal whose sulphate is insoluble, with sulphuric acid or a soluble sulphate.

Zinc and iron give hydrogen and a sulphate when treated with sulphuric acid :

$$Zn + H_2SO_4 = ZnSO_4 + H_2 ;$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

This kind of action takes place whenever a metal is dissolved in sulphuric acid at the ordinary temperature. If, however, the temperature is raised the displaced hydrogen acts upon some of the sulphuric acid, or the metal extracts some of the oxygen of the acid, reducing it partly to sulphurous acid, when sulphur dioxide is given off. This happens in the case of copper, as has been pointed out. It may be represented either by these equations :

$$Cu \quad + H_2SO_4 = CuSO_4 + H_2 ;$$
$$H_2SO_4 + 2H \quad = SO_2 \quad + 2H_2O ;$$

or by these :

$$Cu \; + H_2SO_4 = CuO \quad + SO_2 + H_2O ;$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

The action of sulphuric acid on metallic hydroxides has been fully described.

Most sulphates are soluble in water. The sulphates of barium, strontium, and lead are insoluble in water, and the sulphate of calcium is difficultly soluble. Therefore, if sulphuric acid or a soluble sulphate is added to a solution containing either of the metals, barium, strontium, or lead, a precipitate is formed. A precipitate is also formed when a concentrated solution of a calcium salt is treated in the same way.

When heated with charcoal in the reducing flame of the blow-pipe, sulphates are reduced to sulphides:

$$K_2SO_4 + 4C = K_2S + 4CO, \text{ or}$$
$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

*Sulphites* are made from sodium or potassium sulphite, which are made by treating sodium or potassium hydroxide in solution with sulphur dioxide:

$$2NaOH + SO_2 = Na_2SO_3 + H_2O.$$

All sulphites are decomposed by the common acids, sulphur dioxide being given off:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

The sulphites are changed to sulphates by oxidation. Thus, sodium sulphite is changed to the sulphate when its solution is allowed to stand in contact with the air:

$$Na_2SO_3 + O = Na_2SO_4.$$

The sulphites, like the sulphates, are reduced to sulphides.

**Carbonates.**—Many carbonates are found in nature, some of them in great abundance and widely distributed. The principal one is calcium carbonate. They are made by passing carbon dioxide into solutions of hydroxides, and by adding soluble carbonates to solutions of salts containing metals whose carbonates are insoluble.

The formation of carbonates by the action of carbon dioxide on a solution of hydroxide is illustrated in the case of potassium hydroxide:

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

The formation of calcium carbonate takes place in the same way, but the carbonate formed is insoluble:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

If in either case the action is continued, the normal carbonate first formed is converted into acid carbonate:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3;$$
$$CaCO_3 + CO_2 + H_2O = \left.\begin{matrix} Ca \\ H_2 \end{matrix}\right\} (CO_3)_2.$$

All normal carbonates except those of the members of the potassium family are insoluble, and are decomposed by heat into carbon dioxide and the oxide of the metal. The decomposition of calcium carbonate into lime and carbon dioxide is an example:

$$CaCO_3 = CaO + CO_2.$$

When a soluble carbonate is added to a solution of a calcium, barium, or strontium salt, the corresponding insoluble carbonates are precipitated. When a magnesium salt is treated with a soluble carbonate, however, a basic carbonate is precipitated:

$$4MgSO_4 + 3Na_2CO_3 + 2H_2O = Mg_4(OH)_2(CO_3)_3 + 3Na_2SO_4 + H_2SO_4.$$

This salt, which at first sight appears to be quite complicated, is in all probability derived from three molecules of carbonic acid and four of magnesium hydroxide, as represented in the formula on page 388. Many other metals give basic carbonates under the same conditions. Further, some of the metals, like aluminium, chromium, and tin do not form salts with carbonic acid. If, therefore, salts of these metals are treated with soluble carbonates, the oxides or hydroxides are thrown down, and not the carbonates.

**Phosphates.**—Calcium phosphate is very abundant in nature, and a few other phosphates are also found. The methods used for making phosphates are the same as those used in making salts in general.

The normal phosphates of all the metals except the members of the potassium family are insoluble in water. The normal phosphates, as a rule, are not changed by heat. The secondary phosphates, such as secondary

sodium phosphate, $HNa_2PO_4$, lose water when heated, and yield pyrophosphates :

$$2HNa_2PO_4 = Na_4P_2O_7 + H_2O.$$

Sodium
pyrophosphate.

Those phosphates in which only one third of the hydrogen is replaced by metal—as, for example, primary sodium phosphate, $H_2NaPO_4$—lose water when heated, and yield metaphosphates :

$$H_2NaPO_4 = NaPO_3 + H_2O.$$

Sodium
metaphosphate

Neither the pyrophosphates nor the metaphosphates are changed by heat.

**Silicates.**—The silicates, as has been stated, are very widely distributed in nature. Those which are most abundant are the *feldspars* and their decomposition-products. The principal feldspar is a complex silicate of aluminium and potassium, of the formula $KAlSi_3O_8$, derived from the polysilicic acid $H_4Si_3O_8$, which is formed from three molecules of normal silicic acid by the loss of four molecules of water :

$$3Si(OH)_4 = H_4Si_3O_8 + 4H_2O.$$

Silicates can be made by heating together, at a high temperature, silicon dioxide, in the form of sand, and basic oxides or carbonates :

$$CaO \quad + SiO_2 = CaSiO_3 ;$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Only the silicates of the members of the potassium group are soluble in water. When these are treated in solution with dilute acids, they are decomposed, as has been explained under Silicic Acid (which see).

Some silicates, which are insoluble in water, are decomposed by the ordinary acids, such as sulphuric and hydrochloric acids, the silicic acid separating as a difficultly soluble substance, which, if dried on the water-bath, becomes insoluble.

Many silicates, which are not acted upon by strong acids, are decomposed by fusion with sodium or potassium carbonate, when the silicate of potassium or sodium and the oxide of the metal contained in the silicate are formed. Silicates which are not decomposed in either of the ways mentioned, yield to hydrofluoric acid. The action consists in the formation of the gas, silicon tetrafluoride, $SiF_4$, and the fluorides of the metals present. Thus, the reaction in the case of feldspar takes place in accordance with the equation,

$$KAlSi_3O_8 + 16HF = KF + AlF_3 + 3SiF_4 + 8H_2O.$$

The silicon fluoride is given off as a gas, and the fluorides formed are soluble in water. Hence, hydrofluoric acid is said to dissolve the silicates.

# CHAPTER XXV.

## ELEMENTS OF FAMILY I, GROUP A:
### THE ALKALI METALS :—LITHIUM—SODIUM—POTASSIUM—RUBIDIUM—CÆSIUM—AMMONIUM.

**General.**—The elements of this group which are most abundant in nature are sodium and potassium. While lithium occurs in considerable quantity, the two remaining elements, rubidium and cæsium, have been found in only very small quantities. They are all strongly basic, their hydroxides being the strongest bases known. They form well-characterized salts with all acids, and as a rule their salts are very stable. In all their compounds they act as univalent elements, except in those which they form with hydrogen, and in their peroxides; in the latter they appear to be bivalent. Leaving these compounds out of consideration the general formulas of some of the other principal compounds are as follows:

$MCl$, $M_2O$, $M_2S$, $M(OH)$, $M(SH)$, $MNO_3$, $M_2SO_4$, etc.

The valence of the members of the group towards other elements is, in general, constant.

The relations between the atomic weights are interesting. That of sodium, 22.82, is very nearly half the sum of those of lithium, 6.97, and potassium, 38.82. We have

$$\frac{6.97 + 38.82}{2} = 22.89.$$

So, also, that of rubidium, 84.78, is approximately half the sum of those of potassium, 38.82, and cæsium, 131.89.

$$\frac{38.82 + 131.89}{2} = 85.35.$$

The specific gravity of these elements increases with the atomic weight; and their melting-points become lower as the atomic weights become higher.

|  | At. Wt. | Sp. Grav. | M. P. |
|---|---|---|---|
| Lithium, . . . | 6.97 | 0.594 | 180°. |
| Sodium, . . . | 22.82 | 0.972 | 95.6° |
| Potassium, . . | 38.82 | 0.865 | 62.5° |
| Rubidium, . . | 84.78 | 1.52 | 38.5° |
| Cæsium, . . . | 131.89 | ? | ? |

The regularity is complete in the case of the melting-points, but as regards the specific gravities sodium is an exception to the rule. As sodium and potassium and their compounds are much more commonly met with than the other members of the group, these will form the chief subject of consideration in this chapter.

## Potassium, K (At. Wt. 38.82).

**Occurrence.**—Potassium is a constituent of many minerals, particularly of feldspar, the common variety of which, as has already been explained, is a complex silicate of aluminium and potassium. It is found also in combination with chlorine as carnallite and sylvite; with sulphuric acid and aluminium, as alum; with nitric acid, as saltpeter or potassium nitrate; and in other forms. The natural decomposition of minerals containing potassium gives rise to the presence of this metal in various forms of combination everywhere in the soil. It is taken up by the plants; and, when vegetable material is burned, the potassium remains behind, chiefly as potassium carbonate. When wood-ash is treated with water the potassium carbonate is dissolved, and it can be obtained in an impure state by evaporating the solution. The substance thus obtained is called *potash*. In the juice of the grape there is contained a salt of potassium, monopotassium tartrate, which is deposited in large quantity from wine. This is commonly called "crude tartar."

**Preparation.**—Potassium was first prepared by Davy in the year 1807, by the action of a powerful electric current on potassium hydroxide. It is now prepared by

heating to a high temperature a mixture of potassium carbonate and carbon :

$$K_2CO_3 + 2C = 2K + 3CO.$$

Such a mixture is best obtained by heating in a closed vessel ordinary mono-potassium tartrate obtained from wine. This contains some calcium tartrate. When the whole is heated decomposition takes place, and there is left behind an intimate mixture of potassium carbonate, calcium carbonate, and charcoal. This mixture is placed in a wrought-iron retort which is connected with a closed flat receiver of sheet-iron. The retort is then heated to a high temperature. The metal distils over into the closed receiver, and at the end of the operation the receiver is placed under petroleum to protect it from the action of the air. The metal obtained in this way is not pure. It can be partly purified by melting it under petroleum and pressing it through a linen bag. It can also be purified, and more completely, by distilling it from a wrought-iron retort.

**Properties.**—Potassium is a light substance, which floats on water. Its freshly cut surface has a bright metallic lustre, almost white ; it acts energetically upon water, causing the evolution of hydrogen, which, together with some of the potassium, burns, while potassium hydroxide is formed at the same time. This reaction has been studied in connection with hydrogen. In consequence of its action upon water, potassium cannot be kept in the air. It is kept under some oil, as petroleum, upon which it does not act. In an atmosphere upon which it does not act, as, for example, hydrogen, it can be distilled. Its vapor is green. Its specific gravity is 0.865 ; its melting-point 62.5°. It combines with chlorine and bromine with great energy, and has the power to extract chlorine from its compounds. It can, therefore, be used for the purpose of isolating some elements, as, for example, magnesium and aluminium, whose oxygen compounds cannot be reduced by the ordinary methods. As, however, sodium is generally used for this purpose instead of potassium, on account of its lower

price, the action will be referred to more at length under Sodium. Although the metal is converted into vapor, no reliable determination of the specific gravity of the vapor has been made, for the reason that the vessels which have been used for the purpose have always been acted upon, and the results thus vitiated.

**Potassium Hydride, $K_2H$.**—This compound is formed by heating potassium in an atmosphere of hydrogen at about 300°. It is a silver-white mass with a metallic lustre. It takes fire in the air. When heated, it begins to dissociate at 200°.

Potassium $\begin{cases} \textbf{Fluoride, KF} \\ \textbf{Chloride, KCl} \\ \textbf{Bromide, KBr} \\ \textbf{Iodide, KI} \end{cases}$ .—Of these salts the only

one which occurs in nature in quantity is the chloride. This is found in the great salt deposits at Stassfurt, Germany, and in some other localities in the form of the mineral *sylvite*, which is more or less impure potassium chloride. It is also found in the form of a compound containing magnesium, potassium, and chlorine, of the formula $MgCl_2.KCl + 6H_2O$, or $KMgCl_3 + 6H_2O$, known as *carnallite*.

The other salts of the group are made by the general methods for making salts, that is, by neutralizing the acids with the hydroxide or carbonate of potassium. It is, however, easier to make the iodide by other methods, and as there is a large demand for this salt for use in medicine and in the art of photography, several methods have been devised for its preparation. Of these, two may serve as examples: (1) The first consists in treating a solution of potassium hydroxide with iodine until it begins to show a permanent yellow color, which is an indication that no more iodine will be taken up. The action is the same as that which takes place when chlorine acts upon warm concentrated caustic potash. Both the iodide and iodate are formed:

$$6KOH + 6I = 5KI + KIO_3 + 3H_2O.$$

By evaporating the water and heating the residue with very finely powdered charcoal, the iodate is decomposed

into iodide and oxygen. The reduction of the iodate takes place in accordance with the equation:

$$2KIO_3 + 3C = 2KI + 3CO_2.$$

(2) Another method employed in the preparation of potassium iodide consists in treating iron filings under water with iodine. Both the iron and iodine dissolve, forming ferrous iodide, $FeI_2$. If to the solution of this compound half as much iodine is added as has already been used in its preparation, ferroso-ferric iodide, $Fe_3I_8$, is formed and remains in solution. By adding a solution of potassium carbonate to this, reaction takes place as represented in the equation:

$$Fe_3I_8 + 4K_2CO_3 + 4H_2O = 8KI + Fe_3(OH)_8 + 4CO_2.$$

The hydroxide of iron is insoluble, and can be removed by filtration.

The fact that the specific gravity of hydrofluoric acid at a low temperature corresponds to the formula $H_2F_2$ makes it not improbable that potassium fluoride has the formula $K_2F_2$. This appears still more probable from the fact that there is an acid potassium fluoride of the formula $KHF_2$, or $KF + HF$. Similar acid salts have not been obtained from the other acids of the group.

**Properties.**—All these salts are soluble, and crystallize well in cubes. The fluoride is the most easily soluble in water. If deposited from a water solution at the ordinary temperature the crystals contain two molecules of water of crystallization, and are deliquescent. The iodide is soluble in 0.7 parts of water at the ordinary temperature, and is also soluble in alcohol (40 parts). The bromide requires about $1\frac{1}{2}$ parts of water for solution at the ordinary temperature, and is but slightly soluble in alcohol. The chloride is soluble in 3 parts of water at the ordinary temperature, and is insoluble in alcohol. All are decomposed by sulphuric acid. The fluoride gives hydrofluoric acid; the chloride gives hydrochloric acid. The bromide gives hydrobromic acid, which acts upon the sulphuric acid, giving sulphur di-

oxide and free bromine (see Hydrobromic Acid). The action in the case of the iodide is more complicated for the reason that hydriodic acid is less stable than hydrobromic acid, and, as it gives up hydrogen very easily, it causes deeper-seated decomposition of the sulphuric acid (see Hydriodic Acid). Potassium iodide in solution takes up iodine readily, and a compound of the formula $KI_3$ can be isolated from a very concentrated solution. No similar compounds of chlorine, bromine, and fluorine are known.

All the salts of this group combine readily with the fluorides, chlorides, bromides, and iodides of the metallic elements in general, forming salts, of which the double fluorides and double chlorides are examples. The relations between these salts and the ordinary oxygen salts have already been discussed to a sufficient extent (see pp. 465 and 466). Those containing fluorine have been studied most fully. Good examples are the following :

$$As \begin{cases} F \\ F \\ F \\ F \\ F_2K \end{cases}, \text{ or } AsF_5.KF\,; \quad As \begin{cases} F \\ F \\ F \\ F_2K \\ F_2K \end{cases}, \text{ or } AsF_5.2KF\,;$$

$$Sb \begin{cases} F \\ F \\ F \\ F_2K \\ F_2K \end{cases}, \text{ or } SbF_5.2KF\,; \quad B \begin{cases} F \\ F \\ F_2K \end{cases}, \text{ or } BF_3.KF\,;$$

$$Si \begin{cases} F \\ F \\ F_2K \\ F_2K \end{cases}, \text{ or } SiF_4.2KF.$$

**Applications.**—Potassium chloride is extensively used for the purpose of making other potassium salts, as, for example, the nitrate and carbonate ; the bromide is used in medicine ; the iodide, as stated above, is used in medicine and in photography.

**Potassium Hydroxide, KOH.**—This well-known substance, commonly called caustic potash, is prepared by treating potassium carbonate in solution with calcium hydroxide in a silver or iron vessel. The reaction is based upon the fact that calcium carbonate is insoluble, and that potassium carbonate and calcium hydroxide are soluble :

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

After enough lime has been added, it is found that a little of the liquid taken out of the vessel gives no carbon dioxide when treated with acids. When this point is reached the liquid is drawn off from the deposit of calcium carbonate by means of a siphon. In the preparation on the large scale this is then evaporated down in a bright wrought-iron vessel until it has the specific gravity 1.16. If the evaporation is carried farther the liquid acts upon the iron. Concentration beyond this point must be carried on in silver vessels, upon which potassium hydroxide does not act. Finally, a liquid is obtained which on cooling completely solidifies. While in the molten condition it is generally poured into moulds of cast-iron or of brass, plated with silver, in which it solidifies in the form of the thin sticks found in the market. This substance is generally not pure. It always contains some carbonate formed by the action of the carbon dioxide of the air, and other substances are also present in small quantity. It can be purified by dissolving it in alcohol, in which the impurities are insoluble. The alcoholic solution of the hydroxide is poured off after a time and evaporated to dryness in a silver vessel. The liquid becomes colored in consequence of a partial decomposition of the alcohol, but on melting the residue the color disappears, as the substances formed from the alcohol are thus destroyed. This product is known as "caustic potash by alcohol." Pure potassium hydroxide in solution is easily obtained by the action of potassium upon distilled water.

Potassium hydroxide is a white brittle substance. In contact with the air it deliquesces, and absorbs carbon

dioxide, being completely transformed into potassium carbonate. It is the strongest of the bases. It decomposes the salts of all other bases, even of those which, like sodium and lithium hydroxides, are soluble in water.

Animal substances like the skin are disintegrated by the hydroxide. It has a caustic action. It is interesting to observe that the strongest bases, like the strongest acids, exert this kind of influence on the complex organic compounds which go to make up the tissues of animals. The action is not by any means always of the same kind, and all that can be said in regard to it, of a general character, is that it tends to break down the complex substances to simpler ones. In the molten condition the hydroxide acts as an oxidizing agent. Hydrogen is given up from it, and substances of acid character are formed with which the potassium combines, forming salts.

Instead of potassium hydroxide, the corresponding sodium compound is used wherever this is possible, as the latter is cheaper. The chief application of the potassium compound outside of the laboratory is for making soft-soap. For this purpose fats are boiled with a solution of potassium hydroxide or carbonate.

**Potassium Oxide, K₂O.**—This compound can be made by burning potassium in the air, and heating the residue to a high temperature. It is also formed by melting potassium hydroxide and metallic potassium together :

$$2K + 2KOH = 2K_2O + H_2.$$

With water it forms the hydroxide, with a marked evolution of heat :

$$K_2O + H_2O = 2KOH.$$

Potassium also forms other oxides of which the *peroxide* of the formula $K_2O_4$ is the best studied. This peroxide is the final product of the combustion of potassium in the air or in oxygen. At a high temperature it breaks down into potassium oxide, $K_2O$, and oxygen. It also gives up its oxygen very readily to substances which are

capable of oxidation, acting so energetically upon some as to cause evolution of light.

**Potassium Hydrosulphide, KSH,** is analogous to potassium hydroxide. Just as the latter is made by the action of potassium on water, so the former can be made by the action of potassium on hydrogen sulphide:

$$K_2 + 2H_2S = 2KSH + H_2.$$

It is, however, obtained most readily by the action of hydrogen sulphide on a solution of potassium hydroxide:

$$KOH + H_2S = KSH + H_2O.$$

When exposed to the action of the air it is oxidized, and becomes colored in consequence of the formation of the disulphide. The action takes place as represented thus:

$$2KSH + O = K_2S_2 + H_2O.$$

**Potassium Sulphide, K₂S,** is made by the reduction of potassium sulphate either by means of hydrogen or carbon. It is thought by some to be present in a solution prepared by saturating a given quantity of potassium hydroxide with hydrogen sulphide, and then adding the same quantity of potassium hydroxide to the product. The formation is supposed to take place as represented in the equations

$$KOH + H_2S = KSH + H_2O;$$
$$KSH + KOH = K_2S + H_2O.$$

This is the action which we should expect, as hydrogen sulphide acts like an acid, and with a strong base we should expect it to form two salts, the acid salt KSH and the neutral salt K₂S. From thermo-chemical investigations of this subject, however, the conclusion appears to be justified that the salt K₂S does not exist in solution, but that it breaks down with water, forming the hydrosulphide and hydroxide:

$$K_2S + H_2O = KSH + KOH.$$

This reaction is analogous to that of water on the oxide:

$$K_2O + H_2O = 2KOH.$$

The *polysulphides of potassium* are compounds having the composition expressed by the formulas $K_2S_2$, $K_2S_3$, $K_2S_4$, and $K_2S_5$. They are formed in general by the action of sulphur on a solution of the hydrosulphide or of the simple sulphide. The disulphide is also formed as explained above by oxidation, when a solution of the hydrosulphide is allowed to stand exposed to the air. They are all colored substances, which readily give up sulphur. If treated with dilute acids each one gives up sufficient sulphur to reduce it to the simple form $K_2S$. If the air is allowed to act upon them for a sufficient length of time they all yield the thiosulphate, $K_2S_2O_3$, the action taking place as represented in the following equations :

$$K_2S_2 + 3O = K_2S_2O_3 ;$$
$$K_2S_3 + 3O = K_2S_2O_3 + S ;$$
$$K_2S_4 + 3O = K_2S_2O_3 + 2S ;$$
$$K_2S_5 + 3O = K_2S_2O_3 + 3S.$$

The fact that no higher sulphide of potassium than the pentasulphide exists, suggests that the action of sulphur upon the monosulphide is analogous to that of oxygen, and that the pentasulphide is analogous to the sulphate :

$$K_2S + 4O = K_2SO_4 ;$$
$$K_2S + 4S = K_2SS_4, \text{ or } K_2S_5.$$

According to this view, the pentasulphide is the salt of a tetrathiosulphuric acid, $H_2SS_4\left(S_2S{<}{SH \atop SH}\right)$, or hydrogen pentasulphide, $H_2S_5$.

The substance used in medicine under the name of *liver of sulphur* or *Hepar sulfuris* is a brown mass formed by melting together potassium carbonate and sulphur, and consisting of polysulphides of potassium and potassium thiosulphate and sulphate. The chief reaction involved is the one represented in the equation

$$3K_2CO_3 + 8S = 2K_2S_3 + K_2S_2O_3 + 3CO_2.$$

If the mass is ignited the thiosulphate is decomposed, forming the sulphate and pentasulphide:

$$4K_2S_2O_3 = 3K_2SO_4 + K_2S_5.$$

Potassium sulphide combines with the sulphides of arsenic, antimony, and tin, forming salts of sulpho-acids. Among the best known of these are the following:

*Potassium Sulpharsenate*, $K_3AsS_4 + H_2O$. — This is formed by treating arsenic pentasulphide or the trisulphide and sulphur with potassium hydrosulphide:

$$6KSH + As_2S_5 = 2K_3AsS_4 + 3H_2S \; ;$$
$$6KSH + As_2S_3 + 2S = 2K_3AsS_4 + 3H_2S.$$

It is also formed by saturating a solution of potassium arsenate with hydrogen sulphide.

*Potassium sulphantimonate*, $K_3SbS_4 + 4\frac{1}{2}H_2O$, and *potassium sulpharsenite*, $KAsS_2 + 2\frac{1}{2}H_2O$, are also easily made. The latter is plainly the analogue of the metarsenite, $KAsO_2$,—metarsenious acid being derived from normal arsenious acid by elimination of one molecule of water:

$$H_3AsO_3 = HAsO_2 + H_2O.$$

**Potassium Nitrate, $KNO_3$.**—This salt is commonly called *saltpeter*. Its occurrence in nature has already been spoken of under Nitric Acid (which see). When refuse animal matter is left to undergo decomposition in the presence of bases nitrates are always the end-products. They are consequently found very widely distributed in the soil. In the East Indies the potassium nitrate formed in the neighborhood of dwellings and stables is collected, and sent into the market. The process of nitrification is carried on artificially on the large scale in the so-called "saltpeter plantations." In these, refuse animal matter is mixed with earthy material, wood ashes, etc., and piled up. These piles are moistened with the liquid products from stables. After the action has continued for two or three years the outer crust is taken off, and extracted with water. The solution thus obtained contains, besides potassium nitrate, calcium and magnesium nitrates. It is treated with a water-extract

of wood ashes or with potassium carbonate, by which the calcium and magnesium are thrown down as carbonates. Much of the saltpeter which is now in the market is made from Chili saltpeter, or sodium nitrate, by treating it with potassium chloride, advantage being taken of the fact that sodium chloride is less soluble in water than potassium nitrate. Molecular weights of sodium nitrate and potassium chloride are dissolved in water and the solution evaporated, when sodium chloride is deposited :

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Potassium nitrate crystallizes in long rhombic prisms, of a salty taste. Under some circumstances it crystallizes in rhombohedrons. When dissolved in water it causes a lowering of the temperature. At ordinary temperatures 100 parts of water dissolve from 20 to 30 parts of the salt; at 100°, 100 parts dissolve 247 parts.

**Applications.**—Potassium nitrate is used as an oxidizing agent in the laboratory, and in the manufacture of fireworks. Its chief use, however, is in the manufacture of gunpowder.

**Gunpowder.**—The value of gunpowder is due to the fact that it *explodes* readily, the explosion being a chemical change accompanied by a sudden evolution of gases. It is a mixture of saltpeter, charcoal, and sulphur. When heated, the saltpeter gives off oxygen and nitrogen; the oxygen combines with the charcoal, forming carbon dioxide and carbon monoxide; and the sulphur combines with the potassium, forming potassium sulphide. When a mixture of saltpeter and charcoal is burned, the reaction which takes place is this :

$$2KNO_3 + 3C = CO_2 + CO + N_2 + K_2CO_3.$$

By adding the necessary quantity of sulphur the carbon dioxide, which would otherwise remain in combination with the potassium as potassium carbonate, is given off, and potassium sulphide formed :

$$2KNO_3 + 3C + S = 3CO_2 + N_2 + K_2S.$$

For this reaction the constituents should be mixed in the proportions :

Saltpeter, . . . . . . . . . . . . 74.83
Charcoal, . . . . . . . . . . . . 13.31
Sulphur, . . . . . . . . . . . . 11.86
                                    ——————
                                    100.00

This is approximately the composition of all powder. When gunpowder explodes, the gases formed occupy about 280 times the volume occupied by the powder itself.

**Potassium Nitrite, KNO₂,** is formed simply by heating the nitrate to a sufficiently high temperature. The reduction is, however, much facilitated by adding to the nitrate some easily oxidized metal, as lead or iron. When the gases formed by the action of arsenic trioxide on nitric acid are passed into potassium hydroxide, both the nitrite and nitrate are formed, and they can be separated by crystallization.

**Potassium Chlorate, KClO₃.**—The character of the reaction by which potassium chlorate is formed when chlorine acts upon a solution of potassium hydroxide has already been discussed (see p. 114). In the manufacture of the chlorate it is found advantageous to make calcium chlorate, and then to treat this with potassium chloride, when, at the proper concentration, potassium chlorate crystallizes out, on account of the fact that it is less soluble than the salts which are brought together. The process in brief consists in passing chlorine into a solution of calcium hydroxide in which an excess of hydroxide is held in suspension. The first action consists in the formation of calcium hypochlorite. When the solution of this salt is boiled it is decomposed, yielding the chlorate and chloride :

$$3Ca(OCl)_2 = Ca(O_3Cl)_2 + 2CaCl_2.$$

On now treating the solution with potassium chloride the following reaction takes place :

$$Ca(O_3Cl)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

Potassium chlorate crystallizes in lustrous crystals of the monoclinic system. Its taste is somewhat like that of saltpeter. It melts at a comparatively low temperature (334°), and at 352° begins to decompose, with evolution of oxygen. At ordinary temperatures 100 parts of water dissolve 6 parts of the salt, and at the boiling temperature 60 parts. In consequence of the ease with which it gives up its oxygen, the chlorate is an excellent oxidizing agent, and it is constantly used in this capacity in the laboratory. Its oxidizing action is well illustrated by grinding a *very little* of it in a mortar with a little sulphur,* when an explosion takes place. With phosphorus the action is exceedingly violent.

The chief uses of potassium chlorate are for the preparation of oxygen, and in the manufacture of matches and fireworks. The tips of Swedish safety matches are made of potassium chlorate and antimony sulphide. The surface upon which they are rubbed to ignite them contains red phosphorus. The chlorate is frequently used in medicine, particularly as a gargle in cases of sore throat.

**Potassium Perchlorate, $KClO_4$,** is formed in the first stage of the decomposition of the chlorate by heat, as was explained under Oxygen (which see). It is prepared best by heating the chlorate in an open vessel until, after having been liquid, it begins to get solid again. As the salt is difficultly soluble in water, the residue is powdered and washed with water to remove the chloride, and then crystallized from water. Owing to the difficult solubility of this salt it is utilized in chemical analysis for detecting the presence of potassium. For this purpose a solution of perchloric acid is added to the solution under examination, and, if a precipitate is formed, the presence of potassium may be inferred. When heated to about 400° the perchlorate gives up its oxygen, and is reduced to the chloride. It is used to some extent in the manufacture of fireworks, instead of the chlo-

* Great care should be taken with all experiments with potassium chlorate. See description of experiments.

rate, which, owing to its greater instability, is more dangerous.

**Potassium Periodate, KIO₄**, is formed by the action of chlorine on a mixture of potassium hydroxide and potassium iodate. As has been stated in discussing the acids of iodine, this salt is only one form of a group of potassium salts called periodates, all of which are closely related to the normal acid, $I(OH)_7$. Among these salts, for example, are the *mesoperiodate*, $K_3IO_5 + 4H_2O$, and the *diperiodate*, $K_4I_2O_9 + 9H_2O$. The former is a salt of the acid $H_3IO_5$, which is derived from the normal acid by loss of water, thus :

$$I(OH)_7 = H_3IO_5 + 2H_2O.$$

Diperiodic acid is derived from the normal acid as represented in this equation :

$$2I(OH)_7 = H_4I_2O_9 + 5H_2O.$$

**Potassium Cyanide, KCN.**—Under Cyanogen it was stated that when nitrogen is passed over a highly heated mixture of carbon and potassium carbonate, potassium cyanide is formed ; and that carbon containing nitrogen compounds, as animal charcoal, when ignited with potassium carbonate, reduces the carbonate, forming potassium, in presence of which the carbon and nitrogen combine, forming the cyanide. The simplest way to make the cyanide is by heating potassium ferrocyanide, $K_4Fe(CN)_6$, which is the starting-point in the preparation of all cyanogen compounds. It breaks down first into potassium cyanide and ferrous cyanide, thus :

$$K_4Fe(CN)_6 = 4KCN + Fe(CN)_2.$$

The ferrous cyanide is, however, decomposed by heat into free nitrogen and carbide of iron,

$$Fe(CN)_2 = FeC_2 + N_2 ;$$

so that the complete decomposition of the ferrocyanide is represented by this equation :

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

As part of the cyanogen is lost in this operation, potassium carbonate is commonly added to the ferrocyanide. This acts upon the ferrous cyanide, forming potassium cyanide and ferrous carbonate :

$$Fe(CN)_2 + K_2CO_3 = FeCO_3 + 2KCN.$$

But the ferrous carbonate breaks down under the influence of heat into ferrous oxide and carbon dioxide

$$FeCO_3 = FeO + CO_2 ;$$

and the ferrous oxide then gives up its oxygen to a part of the potassium cyanide, converting it into the cyanate. The complete reaction between the ferrocyanide and carbonate is therefore represented as follows :

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe.$$

The product obtained in this way necessarily contains some of the cyanate, but for ordinary purposes this does no harm. Potassium cyanide is extremely easily soluble in water, and is deliquescent in moist air. When boiled with water it is decomposed, forming potassium formate and ammonia :

$$KCN + 2H_2O = KCO_2H + NH_3.$$

It combines readily with oxygen when in the molten condition, as shown in its action upon ferrous oxide and upon lead oxide (see p. 404). In consequence of this power to combine with oxygen to form the cyanate, it is a valuable reducing agent, and is not unfrequently used in the laboratory in this capacity.

Just as the fluoride, chloride, bromide, and iodide of potassium combine with the fluorides, chlorides, bromides, and iodides of the metallic elements in general, so potassium cyanide combines with the cyanides of the metallic elements, forming the double cyanides. These have generally a composition analogous to that of the double chlorides and of similar compounds. Thus, silver cyanide forms the compound AgCy.KCy or AgKCy$_2$, in which the cyanogen group CN is represented by the symbol Cy, as is customary ; ferrous cyanide forms the

compounds $K_4FeCy_6$, or $4KCy.FeCy_2$, and $K_3FeCy_6$, or $3KCy.FeCy_3$. These double cyanides are for the most part soluble in water; hence potassium cyanide dissolves many deposits of metallic salts. It is frequently used in the laboratory in analytical operations.

**Potassium Cyanate, KCNO.**—The cyanate is formed by oxidation of the cyanide, when this is melted and lead oxide or minium added to the molten mass. It is most easily prepared by heating together potassium ferrocyanide and manganese dioxide. The action consists first in the decomposition of the ferrocyanide, and the subsequent oxidation of the potassium cyanide thus formed. The mass is extracted with alcohol, as the cyanate is decomposed by water even at the ordinary temperature, the products being potassium carbonate and ammonium carbonate:

$$2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

Acids set cyanic acid free from the cyanate, but the acid is at once decomposed by water, thus:

$$CNOH + H_2O = CO_2 + NH_3.$$

**Potassium Sulphocyanate, KCNS.**—Just as potassium cyanide takes up oxygen to form the cyanate, it also takes up sulphur to form the sulphocyanate:

$$KCN + S = KCNS.$$

It is easily prepared by adding sulphur to molten potassium cyanide, or by heating a mixture of dehydrated potassium ferrocyanide, potassium carbonate, and sulphur. It crystallizes particularly well out of its solution in alcohol. It is deliquescent, and when dissolved in water it causes a very considerable lowering of the temperature. Thus, when 500 grams of the salt are mixed with 400 grams of water at the ordinary temperature, the temperature sinks to about $- 20°$. Unlike the cyanate, it is not decomposed by water.

**Potassium Sulphate, $K_2SO_4$.**—This salt occurs in combination with others in nature, particularly in the mineral

*kainite*, which contains the constituents of potassium sulphate, magnesium sulphate, and magnesium chloride, as indicated in the formula $K_2SO_4.MgSO_4.MgCl_2 + 6H_2O$. This occurs in Stassfurt and in Kalusz. Potassium sulphate is used in medicine, and in the preparation of ordinary alum and of potassium carbonate.

**Primary, or Acid, Potassium Sulphate, $KHSO_4$.**—This salt is obtained as a secondary product in the preparation of nitric acid by the action of sulphuric acid upon saltpeter. It occurs in nature in the Grotto del Solfo, near Naples; and is made by treating the neutral salt with concentrated sulphuric acid. When heated above its melting point it gives off water, and is transformed into the disulphate, thus:

$$2KHSO_4 = K_2S_2O_7 + H_2O.$$

When the disulphate is heated in contact with basic oxides it breaks down, forming sulphates. The decomposition is that represented in the equation

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

The nascent sulphur trioxide thus set free acts with great energy upon the oxides which are present. Hence acid potassium sulphate is a valuable agent for the purpose of decomposing some mineral substances which do not readily yield to the ordinary reagents. Its action consists in breaking down into the disulphate and water, the disulphate then further breaking down into normal sulphate and sulphur trioxide. Besides the salt just mentioned, which is known as the disulphate or pyrosulphate, there are some other salts known, which are derived from another form of disulphuric acid. Two good examples are the salts represented by the formulas $K_3H(SO_4)_2$ and $KH_3(SO_4)_2$. The acid from which these are derived has the formula $H_4S_2O_8$. It is to be regarded as derived from two molecules of normal sulphuric acid by elimination of four molecules of water:

$$2S(OH)_6 = H_4S_2O_8 + 4H_2O.$$

The acid probably has the constitution represented thus:

$$(HO)_2OS<^O_O>SO(OH)_2 = H_4S_2O_8.$$

**Sulphites.**—When sulphur dioxide is passed into a solution of potassium carbonate until carbon dioxide ceases to escape, *potassium sulphite*, $K_2SO_3$, is formed. If the gas is passed to saturation the product is the primary or *acid sulphite*, $KHSO_3$. If the solution of the carbonate is hot and concentrated, the product is the *disulphite*, $K_2S_2O_5$, which bears to the sulphite the same relation that potassium disulphate bears to the sulphate. It is the salt of an acid of the formula $H_2S_2O_5$, which is disulphurous acid:

$$2H_2SO_3 = H_2S_2O_5 + H_2O;$$

This bears to sulphurous acid the same relation that disulphuric acid bears to sulphuric acid.

**Carbonates.**—The normal salt, $K_2CO_3$, is the chief constituent of wood-ashes. When these are extracted with water the carbonate passes into solution and the salt thus obtained can be purified in a number of ways. The impure salt is known as *potash*. Formerly all the potassium carbonate made was obtained from wood-ashes, but at present not more than half of the supply comes from this source. The other sources are the residues from the manufacture of beet-sugar, potassium sulphate and chloride, and wool-fat. The preparation of the carbonate from the sulphate and chloride is accomplished by the same method as that used in the preparation of sodium carbonate from the chloride. The methods used for this purpose will be treated of under the head of Sodium Carbonate (which see). The salt crystallizes from very concentrated solutions in water. It is deliquescent, and dissolves in water with an evolution of heat, and the solution has a strong alkaline reaction.

**Acid Potassium Carbonate, $HKCO_3$,** is formed by passing carbon dioxide over the normal salt, or into the concentrated aqueous solution of the latter. It is much less easily soluble in water than the normal salt. The dry

salt gives off carbon dioxide and water easily when heated, and is converted into the normal salt:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

The same decomposition takes place when the water solution is heated, and even on evaporation at the ordinary temperature.

**Phosphates.**—Three phosphates of potassium are known: (1) *Tertiary, or normal potassium phosphate,* $K_3PO_4$; (2) *secondary, or di-potassium phosphate,* $K_2HPO_4$; and (3) *primary, or mono-potassium phosphate,* $KH_2PO_4$. There is nothing particularly characteristic about these salts, except the decompositions which the primary and secondary salts undergo when heated. These decompositions have already been referred to (see p. 329 and p. 480).

**Potassium Silicate, $K_2SiO_3$.**—A compound of the definite composition represented by the formula here given has not been prepared. A solution of potassium silicate in water is prepared by dissolving sand or amorphous silicon dioxide in potassium carbonate or hydroxide. It is prepared on the large scale by melting together quartz powder and purified potash. It is known as *water glass,* for the reason that its solution dries in the air, forming a glass-like looking mass. To distinguish it from the water glass made with sodium carbonate or hydroxide it is called *potash water glass.*

<div align="center">

RUBIDIUM, Rb (At. Wt. 84.78).

CÆSIUM, Cs (At. Wt. 131.89).

</div>

Both these elements are widely distributed, but only in small quantities. They generally occur in company with potassium, which they resemble closely. They were discovered by means of the spectroscope by Bunsen and Kirchhoff. The characteristic spectrum of rubidium consists of two dark red lines, and this is the origin of the name rubidium (from *rubidus*, dark red). Cæsium was found in the Dürkheim mineral water, and was recognized by two characteristic blue lines, and the name cæsium was given to it on this account (from *cœsius,*

sky-blue). Rubidium is found in different varieties of mica, known as lepidolite. The mineral *pollux*, which is essentially a silicate of cæsium and aluminium, contains cæsium as one of the chief constituents.

It is a remarkable fact that the elements rubidium and cæsium which are so similar to potassium accompany it so generally in nature. Similar facts were noted in the group consisting of chlorine, bromine, and iodine, and that of sulphur, selenium, and tellurium. It will be remembered that chlorine is frequently accompanied by bromine and iodine; and sulphur by selenium and tellurium; but that chlorine and sulphur are present in much larger quantities than the elements which accompany them. Further, the relations between the atomic weights of the members of each group are approximately the same.

**Rubidium** is prepared by the same method as that used in the preparation of potassium.

It is silver-white with a yellowish tint. It can be converted into vapor which has a blue color. It takes fire in the air at the ordinary temperature. Its action upon water is the same as that of potassium, and its salts are very similar to those of potassium.

**Cæsium** has not yet been isolated. By subjecting the chloride to the action of a powerful electric current globules of metal are given off at one of the poles, but these take fire in contact with the air at the ordinary temperature. The salts of cæsium are much like those of rubidium and potassium.

<div align="center">

SODIUM, Na (At. Wt. 22.82).

</div>

**Occurrence.**—Sodium occurs very widely distributed and in large quantities in nature, principally as sodium chloride. It is found in a number of silicates, and is a constituent of plants, especially of those which grow in the neighborhood of the sea-shore and in the sea. Just as the ashes of inland plants are rich in potassium carbonate, so the ashes of sea plants and those which grow near the sea are rich in sodium carbonate. It is found everywhere in the soil, but generally in small quantities.

Its presence in the soil is due to the decomposition of minerals containing it, such as soda feldspar, or albite. It occurs also as sodium nitrate or Chili saltpeter, and in large quantity in Greenland in the form of *cryolite*, which, as has been explained, is a so-called double fluoride of aluminium and sodium, of the formula $Na_3AlF_6$, or $AlF_3.3NaF$.

**Preparation.**—It is prepared from sodium carbonate by the same method as that used in the preparation of potassium, the reaction involved being represented thus :

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

The reduction takes place more readily than in the case of potassium, and it is not necessary to prepare the mixture of carbonate and charcoal by heating the salt of an organic acid, as is done in the preparation of potassium. The carbonate is mixed with charcoal, or powdered anthracite coal, and calcium carbonate, and sometimes this mass is mixed with an oil and then ignited in a crucible.

A successful method for the preparation of sodium on the large scale has been devised by Castner. This consists essentially in the reduction of sodium hydroxide by heating it with an intimate mixture of finely divided iron and carbon. The mass is prepared by mixing the iron with molten pitch, allowing it to cool, breaking it into pieces, and heating to a comparatively high temperature without access of air. The reduction is said to take place at a temperature of 825°, instead of 1400° as in the older method. The main reaction is represented by this equation :

$$6NaOH + FeC_2 = 2Na_2CO_3 + 6H + 2Na + Fe.$$

The preparation of sodium was formerly of more importance than it is at present, for the separation of aluminium from the compounds found in nature depended upon the preparation of sodium. Methods, depending upon the use of an electric furnace, have been devised for the preparation of aluminium, and the old method involving the use of sodium is no longer employed.

**Properties.**—The properties of sodium are very similar to those of potassium. It is light, floating on water; it has a bright metallic lustre; and at the ordinary temperature it is soft like wax. It decomposes water, but not as readily as potassium does. Its specific gravity is 0.9735; its melting point 95.6°. Its vapor is colorless when seen in thin layers, while thick layers appear purple. When melted and allowed to cool it takes the crystallized form. When exposed to the air it acts upon the moisture, and is converted into the hydroxide.

**Applications.**—It is used for the purpose of isolating some elements whose oxides cannot easily be reduced, as, for example, aluminium, magnesium, and silicon, which are prepared by treating their chlorides with sodium. Silicon, however, as we have seen, is prepared better by treating potassium fluosilicate, $K_2SiF_6$, with sodium. The element is also used, in combination with mercury as sodium amalgam, a substance which affords a ready means of making nascent hydrogen. It also finds constant application in the laboratory for a variety of purposes.

**Sodium Hydride, $Na_2H$,** is formed in the same way as the corresponding compound of potassium, and is in every way similar to it.

**Sodium Chloride, $NaCl$.**—This is the substance which is generally known simply as *salt*, or *common salt*. It occurs very widely distributed, and in immense quantities, in the earth. The most important deposits are those at Wieliczka in Galicia, at Stassfurt and Reichenhall in Germany, and at Cheshire in England. Besides these there are, however, many other deposits in the United States of America, in Africa, and in Asia. As it is easily soluble in water, many springs and streams, as well as lakes and the ocean, contain it. Sea-water contains 2.7 per cent. In some places sodium chloride is taken out of mines in solid form. Frequently, however, water is allowed to flow into cavities in the earth, and to remain for some time in contact with the salt. The solution thus formed is afterward drawn or pumped out of the mine and evaporated by appropriate methods. It is generally

allowed slowly to run down walls made of twigs, so that a large surface of the liquid is exposed to the air. The concentrated solution thus obtained is then evaporated to crystallization by the aid of heat.

In hot countries salt is obtained by the evaporation of sea-water, the heat of the sun being used for the purpose. Large shallow cavities are made in the earth, and into these the water flows at high-tide, or it is pumped up into them if they are too high. The process is continued for some months, and then the mother-liquor is drawn off, and the accumulated salt collected and subjected to proper methods of purification.

The salt obtained by the above methods is not pure. It always contains sodium sulphate, together with magnesium and calcium chlorides. The chlorides of magnesium and calcium cause it to become moist in the air. Pure salt does not attract moisture.

Sodium chloride crystallizes in colorless and transparent cubes. Some of that which occurs in nature has a blue color. When deposited from an evaporating solution it takes the form of small cubes arranged in groups of the shape of hollow pyramids, known as the hopper-shaped deposits. If urea or boric acid is present in the solution the crystals of sodium chloride are octahedrons or combinations of these with cubes. When deposited, the crystals enclose water, not as water of crystallization, and this is given off when the crystals are heated, the action being accompanied by a crackling sound. This is known as *decrepitation.*

Sodium chloride melts at 776°, and is volatile at a red heat. In hot water it is but little more soluble than in cold. At 100° 100 parts of water dissolve 39 parts, and at ordinary temperatures 36 parts.

Sodium chloride is the starting-point in the preparation of all sodium compounds, as well as of chlorine and hydrochloric acid. Salt is necessary to the life of man and many other animals. The rôle played by it in the animal economy is not understood, but it is found generally distributed throughout the body in small quantity.

The *fluoride, bromide,* and *iodide* of sodium are like the corresponding potassium salts and need not be described.

**Sodium Hydroxide, NaOH.**—This compound resembles potassium hydroxide in all respects. Being cheaper it is used much more extensively. It is prepared in the same way, by treating sodium carbonate in solution with calcium hydroxide, when insoluble calcium carbonate and soluble sodium hydroxide are formed :

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

The substance is commonly called *caustic soda.* It is extensively used for the purpose of making soap from fats.

**Oxides.**—Sodium forms two oxides, the monoxide, $Na_2O$, and the peroxide, $Na_2O_2$. In this respect a difference is noticed between sodium and potassium ; the latter forming the compounds $K_2O$ and $K_2O_4$.

**Sodium Peroxide, $Na_2O_2$,** has acquired importance in the arts as a bleaching-agent. It is prepared by heating sodium in a current of dry air at a temperature of 300°. When heated to a high temperature it gives off oxygen. Water decomposes it, forming sodium hydroxide, and setting oxygen free.

The *hydrosulphide* and the *sulphides* of sodium are made just as the potassium compounds are, and resemble them very closely.

**Sodium Sulphantimonate, $Na_3SbS_4$,** also known as Schlippe's salt, is a particularly beautiful example of the salts of sulpho-acids. It is made, as its composition indicates, by dissolving antimony pentasulphide in a solution of sodium sulphide :

$$Sb_2S_5 + 3Na_2S = 2Na_3SbS_4.$$

**Sodium Nitrate, $NaNO_3$.**—This compound occurs in large quantity in southern Peru on the border of Chili, and is known as Chili saltpeter. The natural salt contains, besides the nitrate, sodium chloride, sulphate, and iodate. Sodium nitrate is very similar to potassium nitrate, but it cannot be used in place of the more expensive potassium salt in the manufacture of the finer

grades of gunpowder, as it becomes moist in the air, and does not decompose quickly enough. It is used extensively in the manufacture of nitric acid, and also for the purpose of preparing ordinary saltpeter. The iodine contained in Chili saltpeter is now extracted on the large scale, and this forms an important source of iodine.

**Sodium Sulphate, $Na_2SO_4$.**—This salt was first made by Glauber, as it is now made, by the action of sulphuric acid on sodium chloride. It is commonly called Glauber's salt. It occurs in a number of natural waters, as in that of Friedrichshall and Carlsbad. It occurs, further, in solid form in small quantities in some localities. It is made in very large quantities in connection with the manufacture of soda, the first reaction in this process consisting in treating sodium chloride with sulphuric acid. It is also formed in the manufacture of nitric acid by the action of sulphuric acid on Chili saltpeter.

Large quantities of sodium sulphate are now made by the action of magnesium sulphate on sodium chloride. This process is employed at Stassfurt, where both magnesium sulphate and sodium chloride occur in immense quantities. The action takes place between concentrated solutions at low temperatures. It is represented by the equation

$$2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2.$$

It crystallizes in large, colorless, monoclinic prisms, which contain ten molecules of water. These crystals are formed, however, only in case the temperature of the solution is below 33° at the time they are deposited. If a saturated solution is cooled down to a point somewhere between 33° and 40°, the salt is deposited without water of crystallization. When the crystallized salt is heated to 33° it loses a part of its water. The salt is most easily soluble in water at 33°; above this point the solubility decreases. Taking these facts into consideration, it appears probable that in solutions below 33° the compound $Na_2SO_4 + 10H_2O$ is present; while if the solution is heated above this point the compound breaks

down, and the anhydrous salt, as well as the salts with less than ten molecules of water, are less easily soluble. One of the ten molecules of water is held in the compound more firmly than the rest. It seems probable that this is not present as water but as hydroxyl, the salt having the formula $OS \left\{ \begin{matrix} (OH)_2 \\ (ONa)_2 \end{matrix} \right.$ $(=Na_2SO_4 + H_2O)$.

Sodium sulphate easily forms supersaturated solutions which crystallize rapidly if disturbed, if a small crystal of the salt is thrown into them, and if cooled down to $-8°$. This phenomenon is frequently presented by salts, but it is shown in a particularly striking way by this one.

When exposed to the air the salt loses its water of crystallization and crumbles to a white powder. This is the process already described as *efflorescence* (see p. 58).

Sodium sulphate is used as a purgative in medicine, and in the laboratory for the production of cold artificially. A good freezing mixture is made by bringing it together with concentrated hydrochloric acid. Sodium chloride is formed, and the water of crystallization of the sulphate takes the liquid form. This change from the solid to the liquid form is accompanied by a marked absorption of heat. Ice can be made in this way without difficulty. The chief uses of the sulphate are in the manufacture of sodium carbonate and of glass, as will be explained farther on.

**Sodium Thiosulphate, $Na_2S_2O_3 + 5H_2O$.**—This is the salt which is commonly called *hyposulphite of soda*. It is made on the large scale by treating caustic soda with sulphur, and conducting sulphur dioxide into the solution. As has been pointed out, when sulphur acts upon potassium carbonate polysulphides of potassium and the thiosulphate are formed. A similar action takes place when sulphur acts upon caustic soda. The polysulphides in the solution give up sulphur to the sulphite and convert it thus into the thiosulphate:

$$Na_2S_2 + Na_2SO_3 = Na_2S + Na_2S_2O_3.$$

It is also made by boiling a solution of sodium sulphite and adding sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Its chief application is in photography, in which art it is used for the purpose of dissolving the excess of silver salt on the plate which has been exposed to the light, and on which a picture has been developed. The action consists in the formation of salts in which both sodium and silver are contained. These are soluble in water. The thiosulphate will be taken up more in detail under Silver (which see).

**Sodium Carbonate, $Na_2CO_3$.**—This salt, commonly called *soda*, is one of the most important of manufactured chemical compounds. The mere mention of the fact that it is essential to the manufacture of glass and soap will serve to give some conception of its importance. It is found in the ashes of sea plants, just as potassium carbonate is found in the ashes of inland plants. Formerly, it was made entirely from plant ashes, but we are no longer dependent upon this source for our supply of the salt, as two methods have been devised for preparing it from sodium chloride, with which nature provides us in such abundance. As these methods are of great importance, and are, further, very interesting applications of chemical principles, they will be described below.

**Properties.**—Anhydrous sodium carbonate is a powder which is formed by heating the crystallized salt. It melts to a clear liquid when heated to a sufficiently high temperature. It dissolves in water very readily with evolution of heat. The action is, however, not as marked as in the case of potassium carbonate. When the salt is deposited from a water solution it has the composition $Na_2CO_3 + 10H_2O$. This salt, it will be observed, contains the same number of molecules of water of crystallization as sodium sulphate. Like this, too, it effloresces when exposed to the air. When heated it melts in its water of crystallization, and the salt $Na_2CO_3 + H_2O$, or $(HO)_2C(ONa)_2$, separates. This, however, loses water

when heated higher, and is converted into the anhydrous salt. The conduct of the carbonate towards water at different temperatures is suggestive of that of the sulphate. Its maximum solubility is at temperatures between 33° and 70°. Above the latter point the solubility decreases. The cause of this phenomenon is, in all probability, the same as that referred to in describing the analogous phenomenon presented by the sulphate; that is, the existence of the hydrated compound $Na_2CO_3 + 10H_2O$ in solution at temperatures below 70°, and the dissociation of this compound into water and salts containing a smaller number of molecules of water of crystallization, which are less soluble, when the temperature is raised above this point. The crystals of sodium carbonate containing ten molecules of water of crystallization belong to the monoclinic system.

**Applications.**—Sodium carbonate is used in immense quantities in the manufacture of glass, and in the preparation of caustic soda, which is used in the manufacture of soap.

**The Le Blanc Process for the Manufacture of Sodium Carbonate.**—In the manufacture of soda the problem to be solved is to convert sodium chloride into sodium carbonate. The first method devised for this purpose is that of Le Blanc. During the French revolution the supply of potash was cut off from France. This led the government to offer a prize for a practical method for manufacturing soda from common salt. The method proposed by Le Blanc at that time, and which, until recently, has been used almost exclusively involves three reactions:

(1) The sodium chloride is converted into sodium sulphate by treating it with sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

(2) The sodium sulphate thus obtained is heated with charcoal, which reduces it to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

(3) The sodium sulphide is heated with calcium carbonate, when sodium carbonate and calcium sulphide are formed :

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The conversion of the sulphate into the carbonate is, therefore, expressed by the equation

$$Na_2SO_4 + 2C + CaCO_3 = Na_2CO_3 + CaS + 2CO_2.$$

Calcium sulphide is insoluble in water, so that by treating the resulting mass with water the sodium carbonate is separated from the sulphide.

In practice the sodium sulphate is mixed with coal and calcium carbonate, and the mixture heated in appropriately constructed furnaces. The coal reduces the sulphate to sulphide, which then reacts upon the calcium carbonate as above represented. The product of the action is known as *crude soda* or *black ash*. It contains, as its chief constituents, sodium carbonate and calcium sulphide, together with some calcium oxide, and a number of other substances in small quantities. In order to purify this product, it is broken to pieces, and treated with water; and the solution thus obtained evaporated, when the salt of the composition $Na_2CO_3 + 2H_2O$ is deposited. This is dipped out, and dried by heat, when it loses all its water. The product is the *calcined purified soda* of commerce. This always contains some sulphate and chloride together with a small quantity of sulphite.

When dissolved in water and allowed to crystallize, the salt is deposited in large crystals which contain water in the proportion represented by the formula $Na_2CO_3 + 10H_2O$. This is the so-called *crystallized soda.*

Most of the soda which comes into the market is the calcined variety. The mother-liquors from the crystallized soda contain some sodium hydroxide in consequence of the action of calcium hydroxide on sodium carbonate. This can be converted into soda by passing carbon di-

oxide into it; and it can also be partly separated from the carbonate and brought into the market as such.

A method has recently been devised for the purpose of avoiding the manufacture and use of sulphuric acid in the soda factories. This consists in passing a hot mixture of sulphur dioxide, air, and steam over sodium chloride. The action which takes place is represented by this equation:

$$2NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2HCl.$$

As, in the manufacture of soda, by the Le Blanc process, the sulphur remains in combination as calcium sulphide, a process, known as the Chance process, has been devised for its recovery. This consists in passing carbon dioxide into the waste, thus liberating hydrogen sulphide; passing this into another portion of the waste, thus converting the calcium sulphide into the hydrosulphide; and then treating this with carbon dioxide, when a gas rich in hydrogen sulphide is given off:

$$CO_2 + CaH_2S_2 + H_2O = CaCO_3 + 2H_2S.$$

By regulating the supply of air the gas is burned either to sulphur dioxide or to sulphur.

**Ammonia Process for the Manufacture of Soda.**—Another process now in extensive use for the manufacture of soda is the so-called ammonia process, or the *Solvay process*. This depends upon the fact that mono-sodium carbonate, $HNaCO_3$, is comparatively difficultly soluble in water. If, therefore, mono-ammonium carbonate, or acid ammonium carbonate, $HNH_4CO_3$, is added to a solution of common salt, acid sodium carbonate, $HNaCO_3$, crystallizes out, and ammonium chloride remains in the solution:

$$NaCl + HNH_4CO_3 = HNaCO_3 + NH_4Cl.$$

When the acid carbonate thus obtained is heated, it gives

off carbon dioxide, and is converted into the normal salt thus :

$$2HNaCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide given off is passed into ammonia, and thus again obtained in the form of acid ammonium carbonate :

$$NH_3 + H_2O + CO_2 = HNH_4CO_3.$$

The ammonium chloride obtained in the first reaction is treated with lime or magnesia, MgO, and the ammonia set free. This ammonia is used again in the preparation of acid ammonium carbonate. The object of using magnesia is to get magnesium chloride, which, when evaporated to dryness and heated, yields magnesia and hydrochloric acid :

$$MgCl_2 + H_2O = MgO + 2HCl.$$

More than half the soda supply of the world is now furnished by the Solvay process.

**Manufacture of Soda from Cryolite.**—As cryolite occurs in nature in large quantities, and can be obtained cheaply, it is used in some places for the manufacture of soda. The reactions involved are :

(1) The action of calcium carbonate upon cryolite at a high temperature, when sodium aluminate, calcium fluoride, and carbon dioxide are formed as represented in the equation

$$Na_3AlF_6 + 3CaCO_3 = 3CaF_2 + Na_3AlO_3 + 3CO_2.$$

(2) The action of carbon dioxide upon the solution of the aluminate, when aluminium hydroxide is precipitated, and sodium carbonate formed which remains in solution :

$$2Na_3AlO_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2Al(OH)_3.$$

After the mixture of cryolite and calcium carbonate, or chalk, has been heated, the mass is treated with water, when the sodium aluminate dissolves, while the calcium fluoride does not. After separating the solution from the insoluble residue, carbon dioxide is passed through it.

**Mono-Sodium Carbonate, Primary Sodium Carbonate, $HNaCO_3$.**—This salt is commonly called "bi-carbonate of soda." It is easily prepared by passing carbon dioxide over the ordinary carbonate dissolved in its water of crystallization:

$$Na_2CO_3 + CO_2 + H_2O = 2HNaCO_3.$$

When heated it gives up carbon dioxide and water, and is converted into the normal salt. As was stated in connection with the ammonia-soda process, primary sodium carbonate is much more difficultly soluble in water than the normal salt. At ordinary temperatures 100 parts of water dissolve about 10 parts of the salt.

It is used in medicine, and extensively in the preparation of soda-water and other effervescing drinks.

**Sodium-Potassium Carbonate, $KNaCO_3 + 12H_2O$,** is an interesting example of a salt of a dibasic acid containing two different metals. It is easily made by mixing solutions of potassium and sodium carbonates, and is obtained in the form of large crystals.

**Phosphates.**—There are three phosphates of sodium just as there are three phosphates of potassium. The point of chief interest presented by them is that the secondary salt, $HNa_2PO_4$, is the one most easily obtained, and is the substance commonly known as sodium phosphate. When a solution of this salt is treated with an excess of sodium hydroxide, and the solution evaporated, *normal* or *tertiary sodium phosphate* crystallizes out. This has the composition $Na_3PO_4 + 12H_2O$. The solution of the latter salt has an alkaline reaction, and when exposed to the air it absorbs carbon dioxide, and is converted into the secondary salt:

$$2Na_3PO_4 + CO_2 + H_2O = 2HNa_2PO_4 + Na_2CO_3.$$

*Secondary sodium phosphate,* $HNa_2PO_4 + 12H_2O$, is easily made by adding sodium carbonate to a solution of phosphoric acid until an alkaline reaction is shown. It is also prepared on the large scale from bone-ash. It forms monoclinic prisms which effloresce in the air.

**Sodium Metaphosphate, NaPO₃,** is formed when the primary phosphate is ignited. There are several modifications of the salt which appear to differ from one another as represented in the formulas $NaPO_3$, $Na_2P_2O_6$, $Na_3P_3O_9$, etc. This relation is called *polymerism;* or substances which have the same composition but different molecular weights are said to be polymeric. Relations of this kind are very common among the compounds of carbon. Among the hydrocarbons mentioned in Chapter XIX, for example, are acetylene, $C_2H_2$, and benzene, $C_6H_6$. There are, further, two other hydrocarbons of the formulas $C_4H_4$ and $C_8H_8$. Plainly these hydrocarbons all have the same percentage composition. They are polymeric in the sense in which that term has been defined.

**Di-sodium Pyro-antimonate, $H_2Na_2Sb_2O_7 + 6H_2O$,** is of special interest because it is insoluble in cold water, and may therefore be used for the purpose of detecting sodium in analysis. It is formed when a solution of the corresponding potassium salt is added to a solution of a sodium salt.

**Sodium Borate.**—Normal boric acid, as we have seen, has the composition $B(OH)_3$, and there are a number of borates derived from this acid by direct replacement of the hydrogen by metals. The salt which boric acid most readily forms with sodium hydroxide or sodium carbonate, however, is that derived from *tetraboric acid,* $H_2B_4O_7$, which is derived from normal boric acid by elimination of water. (See p. 355). This salt is *borax,* which in crystallized form has the composition represented by the formula $Na_2B_4O_7 + 10H_2O$. By adding the required quantity of sodium hydroxide to a solution of borax, and evaporating to crystallization, sodium metaborate, $NaBO_2 + 4H_2O$, is obtained:

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O.$$

The metaborate is decomposed when its solution is exposed to the action of the air. It is thus converted by carbon dioxide into sodium carbonate and borax, or sodium tetraborate.

*Borax* occurs in nature in several lakes in Asia and in Clear Lake, Nevada, in the United.States. It is manufactured by neutralizing, with sodium carbonate, the boric acid found in Tuscany. When heated, borax puffs up, and at red heat it melts, forming a transparent, colorless liquid. The dehydrated salt is known, as *anhydrous* or *calcined borax.* In the molten condition, borax has the power to combine with metallic oxides, and, as many of the double borates thus formed are colored, the salt is used in blow-pipe work for the purpose of detecting certain metals. As it dissolves metallic oxides, it is used in the process of soldering, as it is necessary to have bright, untarnished metallic surfaces in order that the solder shall adhere firmly. The action of molten borax upon metallic oxides is similar to that which takes place when sodium hydroxide acts upon a solution of borax. Borates of the metals are formed together with sodium borate, or double borates in which part of the hydrogen is replaced by sodium and part by other metals.

Borax is extensively used in the manufacture of porcelain and in glass-painting. It is an antiseptic, preventing the decomposition of some organic substances.

**Sodium Silicate, $Na_2SiO_3$.**—Sodium silicate is formed by dissolving silicon dioxide in sodium hydroxide, and can be obtained in crystallized form. It is prepared on the large scale by melting together quartz sand and sodium carbonate in the proper proportions, and by melting together sodium sulphate, quartz sand, and charcoal powder. This substance is commonly known as *water-glass.* It is soluble in water, and, when its solution dries, it leaves a transparent coating on the surface on which it is placed. It is extensively used in the manufacture of artificial stone.

## Lithium, Li (At. Wt. ·6.97).

Lithium occurs in nature in relatively small quantity, chiefly in the minerals lepidolite, petalite, and spodumene, and in many mineral waters. It is also found in

the ashes of a number of plants. It is prepared by the electrolysis of the chloride in the molten condition. The metal is silver-white, and is characterized by its low specific gravity. It acts vigorously upon water, but, if the water is at the ordinary temperature, the hydrogen given off does not take fire. In the air it conducts itself in much the same way that sodium does.

The most characteristic salts of lithium are the *phosphate, carbonate,* and *chloride.*

**Lithium Phosphate, $Li_3PO_4 + \frac{1}{2}H_2O$,** is precipitated when secondary sodium phosphate is added to a solution of a lithium salt. It is very difficultly soluble in water at the ordinary temperature.

**Lithium Carbonate, $Li_2CO_3$,** is also rather difficultly soluble in water, and is deposited when a solution of sodium carbonate is added to a fairly concentrated solution of lithium chloride. It dissolves uric acid, which is insoluble in water, and is therefore used in medicine for the purpose of removing pathological deposits of this acid in the body. For this purpose it is generally administered in the form of a solution in water containing carbon dioxide.

**Lithium Chloride, LiCl,** is peculiar on account of the fact that it is soluble in alcohol and in a mixture of alcohol and ether. In this respect it differs from the chlorides of potassium and sodium, which are insoluble in alcohol. If, therefore, a mixture of the chlorides of the three metals is treated with alcohol, only lithium chloride dissolves; and in this way lithium can be separated from the other metals.

## Ammonium Salts.

Attention has already been called to the marked similarity of the salts of potassium and sodium to those formed by the action of ammonia on the acids, and known as ammonium salts. The most important of these salts will be briefly considered in this connection. A characteristic property of ammonium salts which distinguishes them from the salts of all the metals is their

volatility. When sublimed, they all undergo decomposi-
tion, which is either partial or complete.

The simplest kind of decomposition which they un-
dergo is dissociation into ammonia and the acid. This
is illustrated in the case of ammonium chloride, which,
when heated to a sufficiently high temperature, is dis-
sociated into ammonia and hydrochloric acid. This is
an example of true dissociation. The amount of decom-
position is constant for any given temperature and pres-
sure.

An ammonium salt of a polybasic acid containing some
metal gives off ammonia and leaves an acid salt, which
generally undergoes further decomposition. Thus, so-
dium-ammonium sulphate, $NaNH_4SO_4$, first gives off
ammonia and forms mono-sodium sulphate:

$$SO_4 \left\{ \begin{array}{l} Na \\ NH_4 \end{array} \right. = SO_4 \left\{ \begin{array}{l} Na \\ H \end{array} \right. + NH_3.$$

The acid salt thus formed then undergoes **further**
change and the pyrosulphate is formed:

$$2SO_4 \left\{ \begin{array}{l} Na \\ H \end{array} \right. = Na_2S_2O_7 + H_2O.$$

Another example of this kind of decomposition of am-
monium salts is that afforded by sodium - ammonium
phosphate, $HNaNH_4PO_4$. When heated, this gives off
ammonia and then water, the final product being sodium
metaphosphate:

$$PO \left\{ \begin{array}{l} ONa \\ ONH_4 \\ OH \end{array} \right. = PO \left\{ \begin{array}{l} ONa \\ OH \\ OH \end{array} \right. + NH_3;$$

$$PO \left\{ \begin{array}{l} ONa \\ OH \\ OH \end{array} \right. = PO_2ONa + H_2O.$$

Some ammonium salts undergo deeper-seated decom-
positions, and do not give ammonia as one of the prod-
ucts. This is true especially of such salts as readily
give off oxygen. In such cases the ammonia is oxidized,

so that the hydrogen forms water. This is illustrated in the decomposition of ammonium nitrate and nitrite :

$$NH_4NO_3 = N_2O + 2H_2O \; ; \; and$$
$$NH_4NO_2 = N_2 \quad + 2H_2O.$$

Further, all ammonium salts are decomposed with evolution of ammonia when treated with basic hydroxides. This has been illustrated in the preparation of ammonia from ammonium chloride by treatment with calcium hydroxide :

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The ammonium salts are made by neutralizing acids with ammonia.

**Ammonium Chloride, NH₄Cl.**—This salt is commonly called *sal ammoniac.* At present its principal source is the so-called ammoniacal liquor of the gas-works. This liquid contains a considerable quantity of ammonium carbonate, and, when it is treated with lime, ammonia is given off. This is passed into hydrochloric acid, and the solution of ammonium chloride thus formed evaporated to crystallization. The salt has a sharp, salty taste, and is easily soluble in water. When heated, it is converted into vapor without melting and with very slight decomposition ; and when the vapor comes in contact with a cold surface, it condenses in crystalline form. This process of vaporizing and condensing a solid is called *sublimation.* Some of the ammonium chloride met with in the market has been sublimed. The salt is used in the preparation of ammonia, in medicine, and for other purposes. When it is dissolved in water, a considerable lowering of temperature is caused.

**Ammonium Sulphocyanate, NH₄CNS.**—This salt is prepared by bringing together aqueous ammonia, carbon disulphide, and alcohol. The first product is ammonium thiocarbamate, the formation of which is perfectly analogous to the formation of the ordinary carbamate by the action of carbon dioxide on ammonia :

$$CS_2 + 2NH_3 = CS \begin{cases} NH_2 \\ SNH_4 \end{cases};$$

$$CO_2 + 2NH_3 = CO \begin{cases} NH_2 \\ ONH_4 \end{cases}.$$

The thiocarbamate afterwards breaks down when heated, forming the sulphocyanate and hydrogen sulphide :

$$CS \begin{cases} NH_2 \\ SNH_4 \end{cases} = CNSNH_4 + H_2S.$$

The salt, like so many other ammonium salts, causes a marked lowering of temperature when dissolved in water. When 100 grams are dissolved in the same weight of water at 17°, the temperature falls to $-12°$. It is now much used in analytical processes for the estimation of silver and copper.

**Ammonium Sulphide, $(NH_4)_2S$.**—This compound is extensively used in chemical analysis for the purpose of precipitating those sulphides which are soluble in dilute hydrochloric acid (see p. 198 and p. 473). As will be remembered, in the usual method of analyzing a mixture of substances, the first step consists in adding hydrochloric acid to the solution. This precipitates silver, lead, and, under certain conditions, mercury. This precipitate having been filtered off, hydrogen sulphide is passed through the filtrate, when those metals are precipitated whose sulphides are insoluble in dilute hydrochloric acid. The precipitate is filtered off, and ammonium sulphide added to the filtrate, when the metals whose sulphides are soluble in dilute hydrochloric acid are thrown down. Among these are iron, cobalt, nickel, manganese, etc. Any other soluble sulphide might be used ; but the advantage of ammonium sulphide is that it is volatile, and hence, by evaporating the solution and heating, it can be got rid of after it has served its purpose. Another use to which it is put in analysis is for the purpose of dissolving the sulphides of tin, arsenic, and antimony, which are precipitated by hydrogen sulphide, and thus separating these from the other sulphides of the group. This solution depends upon the

power of the sulphides to form salts of sulpho-acids, as has been repeatedly explained.

Ammonium sulphide is made by passing hydrogen sulphide into an aqueous solution of ammonia. If the gas is passed until the solution is saturated, the product is the hydrosulphide:

$$NH_3 + H_2S = NH_4HS.$$

If only half this quantity of the gas is passed, the product is the sulphide:

$$2NH_3 + H_2S = (NH_4)_2S.$$

The simplest way to make it, however, is to divide a quantity of a solution of ammonia into two equal parts; saturate one half, thus forming the hydrosulphide, and add the other half, when this reaction takes place:

$$HNH_4S + NH_3 = (NH_4)_2S.$$

The product is a colorless liquid of a disagreeable odor. It soon changes color, becoming yellow, and after a time a yellow deposit is formed in the vessel in which it is contained. This change of color is due to the action of the oxygen of the air. Some of the sulphide is decomposed into ammonia, water, and sulphur, thus:

$$(NH_4)_2S + O = 2NH_3 + H_2O + S.$$

The sulphur set free in this way combines with the undecomposed ammonium sulphide, forming the compounds $(NH_4)_2S_2$, $(NH_4)_2S_3$, $(NH_4)_2S_4$, and $(NH_4)_2S_5$. When as much sulphur has been set free as is required to form the pentasulphide, further decomposition by the oxygen of the air causes a deposit of sulphur. Therefore, in bottles containing ammonium sulphide which are allowed to stand for a long time a deposit of sulphur is always found. A solution containing the polysulphides is called *yellow ammonium sulphide.* It is this which is used for the purpose of dissolving the sulphides of arsenic, antimony, and tin in analytical operations.

As stated above, a solution of *ammonium hydrosulphide,* $HNH_4S$, is made by passing hydrogen sulphide into a solution of ammonia until no more is taken up.

**Ammonium Nitrate, $NH_4NO_3$,** is obtained in crystals, which are easily soluble in water. It is of use chiefly in the preparation of nitrous oxide. When heated suddenly to a high temperature it is decomposed rapidly into nitrogen, water, and nitric oxide:

$$2NH_4NO_3 = N_2 + 2NO + 4H_2O.$$

This decomposition may take place in the preparation of nitrous oxide if in the last stages of the operation the heat is raised too high, and explosions may be caused in this way. When dissolved in water a marked lowering of temperature takes place.

**Ammonium Carbonate, $(NH_4)_2CO_3$.**—When dry ammonia gas and dry carbon dioxide are brought together, they unite and form the salt known as *ammonium carbamate*, which has the composition $CO \begin{cases} NH_2 \\ ONH_4 \end{cases}$:

$$CO_2 + 2NH_3 = CO \begin{cases} NH_2 \\ ONH_4. \end{cases}$$

This is the salt of an acid, $CO \begin{cases} NH_2 \\ OH \end{cases}$, known as carbamic acid. When the carbamate is dissolved in water, it is converted into the carbonate:

$$CO \begin{cases} NH_2 \\ ONH_4 \end{cases} + H_2O = CO \begin{cases} ONH_4 \\ ONH_4. \end{cases}$$

When heated to 58°, the normal carbonate is decomposed, forming carbon dioxide, water, and ammonia. The substance found in the market under the name of ammonium carbonate is made by heating together ammonium chloride or sulphate and chalk. It consists of normal ammonium carbonate, $(NH_4)_2CO_3$, primary ammonium carbonate, $HNH_4(CO_3)$, and ammonium carbamate.

*Primary Ammonium Carbonate*, $HNH_4CO_3$, is formed by treating the normal carbonate with carbon dioxide, and by allowing the commercial carbonate to lie exposed to the air, when the carbamate is converted into the carbonate by the moisture, and the carbonate loses ammonia:

$$CO \begin{cases} ONH_4 \\ ONH_4 \end{cases} = CO \begin{cases} OH \\ ONH_4 \end{cases} + NH_3.$$

It is easily decomposed into ammonia, water, and carbon dioxide.

**Sodium-ammonium Phosphate, $HNaNH_4PO_4$.**—This salt is known as *microcosmic salt*, and is much used in the laboratory in blow-pipe work. It is contained in guano and in decomposed urine. It is easily made by mixing solutions of di-sodium phosphate and ammonium chloride, and allowing to crystallize. In crystallized form it contains four molecules of water, $HNaNH_4PO_4 + 4H_2O$. The changes which the anhydrous salt undergoes when heated were described on page 518. When the crystallized salt is heated, the water of crystallization is first given off. The value of the salt in blow-pipe work depends upon the fact that at high temperatures the metaphosphate combines with metallic oxides, forming mixed phosphates, the reactions being like those which metaphosphoric acid undergoes with water :

$$2HPO_3 + H_2O = H_4P_2O_7 ;$$
$$HPO_3 + H_2O = H_3PO_4 ;$$
$$2NaPO_3 + M_2O = Na_2M_2P_2O_7 ;$$
$$NaPO_3 + M_2O = NaM_2PO_4.$$

Many of these double phosphates and pyrophosphates are colored, and, like the double borates (see p. 516) they furnish a means of detecting some of the metals.

**Reactions of the Members of the Sodium Group which are of Value in Chemical Analysis.**—The chief difficulty experienced in chemical analysis is in distinguishing between similar elements. Sodium and potassium, for example, conduct themselves so much alike in so many respects that we might subject them to the influence of a number of reagents without being able to tell which one we are working with. For purposes of analysis, therefore, it is necessary to take advantage of differences between the elements, and the more striking the differences the better. Those reactions which give rise to the formation of insoluble compounds or precipitates are most frequently used in analysis. Very few salts of the members of the sodium

group are insoluble, and the difficulty of distinguishing between these elements is increased by this fact. In ordinary analyses the elements of this group which are of most importance are potassium and sodium, the other elements of the group being but rarely met with. Ammonium compounds are easily distinguished from those of potassium and sodium by the fact that, when treated with caustic soda or potash, they give off ammonia, which is recognized by its characteristic odor. The chief reactions which are of value in distinguishing between potassium and sodium are the following:

*Platinum Chloride*, $PtCl_4$, forms difficultly soluble salts with potassium and ammonium chlorides. These are the *chloroplatinates*, $K_2PtCl_6$ and $(NH_4)_2PtCl_6$. The corresponding salt of sodium is easily soluble.

*Perchloric Acid*, $HClO_4$, forms difficultly soluble *potassium perchlorate*, $KClO_4$, when added to solutions of potassium salts.

*Fluosilicic Acid*, $H_2SiF_6$, forms difficultly soluble salts with potassium and sodium, $K_2SiF_6$ and $Na_2SiF_6$, but not with ammonium.

*Tartaric Acid*, $H_2(C_4H_4O_6)$, forms a difficultly soluble potassium salt of the formula $KH(C_4H_4O_6)$. The corresponding salt of sodium is easily soluble. The formation of mono-potassium tartrate takes place as represented in the equation:

$$KCl + H_2(C_4H_4O_6) = KH(C_4H_4O_6) + HCl.$$

Normal or neutral potassium tartrate is soluble in water, so that, if the difficultly soluble acid tartrate is filtered off, and potassium carbonate added to it, it dissolves in consequence of the formation of the neutral salt, which takes place as represented in the equation

$$2KH(C_4H_4O_6) + K_2CO_3 = 2K_2(C_4H_4O_6) + CO_2 + H_2O.$$

If, to the solution of the neutral salt, hydrochloric acid is added, the acid salt is again formed and precipitated:

$$K_2(C_4H_4O_6) + HCl = KH(C_4H_4O_6) + KCl.$$

*Di-sodium Pyro-antimonate*, $Na_2H_2Sb_2O_7$, is insoluble in cold water, and is formed when a solution of the corre-

sponding potassium salt is added to a solution of a sodium salt.

**Flame Reactions and the Spectroscope.**—When a clean piece of platinum wire is held for some time in the flame of the Bunsen burner, it then imparts no color to the flame. If now a small piece of sodium carbonate or any other salt of sodium is put on it, the flame is colored intensely yellow. All sodium compounds have this power, and hence the chemist makes use of this fact for the purpose of detecting the presence of sodium. Similarly, potassium compounds color the flame violet; lithium compounds color the flame red; rubidium and cæsium produce colors similar to that of the potassium flame. While it is an easy matter to recognize potassium alone, or any one of the other metals alone, it is difficult to do so when they are together in the same compound. For example, when sodium and potassium are together, the intense yellow caused by the sodium completely masks the more delicate violet caused by the potassium, so that the latter cannot be seen by the unaided eye. In this particular case the difficulty can be got over by letting the light from the flame pass through a blue glass, or through a thin vessel of glass containing a solution of indigo. The yellow light is thus cut off, while the violet light passes through and can be recognized. A more general method for detecting the constituents of light is by means of a prism of glass. Lights of different colors, which are produced by ether waves of different lengths, are turned out of their course to different extents when passed through a prism, as is seen when white sunlight is passed through a prism. A narrow beam of white light passing in emerges as a band of various colors, called its *spectrum.* We thus see that white light is made up of lights of different colors; or, to speak in the language of physics, that motion of the light-ether which produces upon the eye the sensation of white light is made up of a number of motions, each of which alone produces upon the eye the sensation of a color. Similarly, we can determine what any light is composed of. Every light has its char-

acteristic spectrum. The light given off from any solid heated to a white heat gives a *continuous spectrum,* like that of the sunlight. An incandescent gaseous substance, on the other hand, gives a spectrum made up of separate bands of color, or a *banded spectrum.* The light produced by burning sodium, or by introducing a sodium compound in a colorless flame, gives a spectrum consisting of a narrow yellow band. The spectrum of the potassium flame consists essentially of two bands, one red and one violet. Further, these bands always occupy definite positions relatively to one another, so that, in looking through a prism at the light caused by potassium and sodium, the yellow band of sodium is seen in its position, and the two potassium bands in their proper positions. There is therefore no difficulty in detecting these elements when present in the same substance or in the presence of other elements which give characteristic spectra.

The instrument used for the purpose of observing the spectra of different lights is called the *spectroscope.** It consists essentially of a prism and two telescopes. Through one of the telescopes the light to be examined is allowed to pass so as to strike the prism properly. The light emerges from the other side of the prism, and is observed through the other telescope, which is provided with lenses for the purpose of magnifying the spectrum. By means of a third telescope, an image of a scale is thrown upon the face of the prism from which the spectrum emerges, and is reflected thence into the observing-tube, together with the spectrum, so that the position of the bands can be accurately determined. By means of the spectroscope, it is possible to detect the minutest quantities of some elements, and, since it was devised, several new elements have been discovered through its aid ; as, for example, cæsium, rubidium, thallium, indium, gallium, and others.

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* For an account of the spectroscope and its uses, the student should consult some work on physics. The principles involved in its construction and application are physical principles, and cannot properly be taken up in detail in a text-book of chemistry.

# CHAPTER XXVI.

### ELEMENTS OF FAMILY II, GROUP A:
### GLUCINUM—MAGNESIUM—CALCIUM—STRONTIUM—BARIUM [ERBIUM].

**General.**—The elements of this group fall into two sub-groups. Calcium, strontium, and barium are strikingly alike. They also have some points in common with the members of the potassium family, and at the same time are related in some degree to the metals of Family III, Group A, which are known as the earth metals. Therefore, calcium, barium, and strontium are generally called the metals of the *alkaline earths*. Glucinum and magnesium resemble the metals of the alkaline earths in some ways, but they also resemble the members of Group B, of the same family, which includes zinc and cadmium. On comparing the group with the elements presented in the last chapter, some analogous facts are noticed. Arranging the five elements of the potassium group in the order of their atomic weights, and the elements of Family II, Group A, in the same way, we have this table :

| Li | Na | K | Rb | Cs |
|------|-------|-------|-------|--------|
| 6.97 | 22.82 | 38.82 | 84.78 | 131.89 |
| Gl | Mg | Ca | Sr | Ba |
| 9.01 | 24.10 | 39.76 | 86.95 | 136.39 |

As regards the analogies between the elements in each group, the general statement can be made that the last three members of each group resemble one another more closely than they resemble the first two members of the group, while the first two members in each group also resemble each other closely. The natural grouping according to the properties is into the sub-groups :

(527)

| a | | b |
|---|---|---|
| Lithium, Sodium, | and | Potassium, Rubidium, Cæsium. |
| Glucinum, Magnesium, | and | Calcium, Strontium, Barium. |

The relations between the atomic weights of the elements of Family II, Group A, are similar to those of the elements of Family I, Group A. That of magnesium, 24.10, is nearly half the sum of those of glucinum, 9.01, and calcium, 39.76. We have

$$\frac{9.01 + 39.76}{2} = 24.38.$$

So, also, that of strontium, 86.95, is approximately half the sum of those of calcium, 39.76, and barium, 136.39 :

$$\frac{39.76 + 136.39}{2} = 88.07.$$

In the calcium group the specific gravities increase in the order of the atomic weights :

|  | At. Wt. | Sp. Gr. |
|---|---|---|
| Calcium, . . . . | 39.76 | 1.57 |
| Strontium, . . . | 86.95 | 2.5 |
| Barium, . . . . | 136.39 | 3.75 |

All the elements of the group are bivalent. The general formulas of the principal compounds are as follows :

$$MCl_2, \ M(OH)_2, \ M(NO_3)_2, \ MSO_4, \ M_3(PO_4)_2, \ MSiO_3, \text{ etc.}$$

The chlorides, hydroxides, and nitrates are soluble in water. The sulphates decrease in solubility as the atomic weights increase. Glucinum sulphate, $GlSO_4$, is soluble in its own weight of water; magnesium sulphate, $MgSO_4$, is soluble in about three times its weight of water; calcium sulphate, $CaSO_4$, dissolves in 400 parts ; strontium sulphate, $SrSO_4$, in about 8000 parts ; and

barium sulphate, $BaSO_4$, in about 400,000 parts of water. Barium sulphate, as will be seen, is practically insoluble in water. The normal carbonates of all except glucinum are insoluble in water. The solubility of the hydroxides increases as the atomic weight increases. Glucinum hydroxide is insoluble; magnesium hydroxide is but slightly soluble. One hundred parts of water at the ordinary temperature dissolve 0.1368 parts of calcium hydroxide, 2 parts of strontium hydroxide, and 3.5 parts of barium hydroxide. The solubility of strontium and barium hydroxides is, however, much increased at higher temperatures.

## CALCIUM SUB-GROUP.

This sub-group, as has been stated, consists of the three very similar elements, calcium, strontium, and barium. Of these calcium occurs most abundantly in nature. Barium and strontium frequently accompany each other, and both are found in some localities in company with calcium. They are much less abundant in nature than calcium.

### CALCIUM, Ca (At. Wt. 39.76).

**Occurrence.**—Calcium is found in nature in enormous quantities, chiefly in the form of the carbonate, $CaCO_3$, as limestone, marble, and chalk. It also occurs in the form of the sulphate, $CaSO_4$, as gypsum; of the phosphate, $Ca_3(PO_4)_2$, as phosphorite and apatite; of the fluoride, $CaF_2$, as fluor-spar. It is found in solution in most natural waters either as the carbonate or sulphate; and in the organs of plants and animals. Bones contain a large proportion of calcium phosphate; egg-shells and coral contain calcium carbonate.

**Preparation.**—The element is made by decomposing molten calcium chloride by means of the electric current; and by first making zinc-calcium and distilling off the zinc by heating to a high temperature in a crucible made of carbon from a gas-retort. The zinc-calcium is made by melting together a mixture of calcium chloride, zinc,

and sodium. The sodium decomposes the chloride, and the reduced metal dissolves in or combines with the zinc as soon as it is formed.

**Properties.**—It is a brass-yellow, lustrous metal, which in moist air becomes covered with a layer of hydroxide and carbonate. At ordinary temperatures it decomposes water just as potassium and sodium do, but heat is not evolved rapidly enough to set fire to the hydrogen. Heated to a high temperature, it burns in the air, forming the oxide. It is not made in quantity, and has found no practical application.

**Calcium Chloride, $CaCl_2$** —This salt is found in nature in combination with other chlorides, particularly in the mineral tachydrite, which occurs in the salt deposits at Stassfurt, and has the composition represented by the formula $CaCl_2.MgCl_2 + 12H_2O$. It is also found in solution in sea-water. It is obtained as a by-product in the preparation of ammonia from ammonium chloride and lime ; in the preparation of potassium chlorate from calcium chlorate and potassium chloride (see p. 494); and in the ammonia-soda process. It is made by dissolving calcium carbonate in hydrochloric acid, as in the preparation of carbon dioxide. From very concentrated solutions it crystallizes with six molecules of water, $CaCl_2 + 6H_2O$. When these crystals are exposed to the air they soon deliquesce. When a solution of calcium chloride is evaporated, and care is taken to keep the temperature below 200°, it solidifies, forming a porous mass which has the composition represented by the formula $CaCl_2 + 2H_2O$. This is much used in laboratories as a drying agent, as it absorbs water with great ease. If this salt is heated above 200° it loses all its water, and the dehydrated chloride melts, forming fused calcium chloride. This is also much used on account of its drying power. Gases are passed through tubes filled with granulated calcium chloride for the purpose of drying them, and the salt is also placed in vessels in which it is necessary that the air should be dry, as in balance-cases, desiccators, etc. The fused salt generally has a slight alkaline reaction, which is caused by the presence of a

small quantity of lime. This is formed by the action of steam at high temperature on the chloride, the reaction being represented by this equation :

$$CaCl_2 + H_2O = CaO + 2HCl.$$

This decomposition takes place only to a slight extent. The porous chloride, which contains two molecules of water, does not contain any hydroxide, and it is therefore better adapted for use in cases in which it is necessary that it should not absorb carbon dioxide, as in the analysis of organic compounds.

Calcium chloride forms crystallized compounds with ammonia and with alcohol, as well as with water. It is obvious from this that calcium chloride cannot be used for the purpose of drying ammonia gas. When the compounds with ammonia and with alcohol are heated they break down, yielding ammonia and alcohol respectively, as the compound with water gives up the latter.

**Calcium Fluoride, $CaF_2$.**—This compound occurs in large quantities in nature as the mineral fluor-spar. It occurs beautifully crystallized in cubes, and is insoluble in water. It is the source of fluorine compounds in general, and is used in metallurgical operations for the reason that it melts readily and does not act upon other substances easily. It therefore simply serves as a liquid medium in which reactions take place at high temperatures. A substance which acts in this way and is used for this purpose is called a *flux*. The name fluorspar has its origin in this use of the substance. A flux plays to some extent the same part at elevated temperature in facilitating reactions that water plays at ordinary temperatures.

**Calcium Oxide, $CaO$.**—This important compound is commonly called *lime*, or, to distinguish it from the hydroxide or *slaked lime*, it is called *quick-lime*. It is made in large quantity by heating calcium carbonate in appropriately constructed furnaces, known as lime-kilns. Pure lime is made by decomposing some pure form of calcium carbonate, as marble or calc-spar. The decomposition of calcium carbonate is not complete in an at-

mosphere of carbon dioxide, hence precautions must be taken to remove the gas formed by the decomposition. Further, when lime is heated to a temperature considerably higher than that necessary to effect the first decomposition it again absorbs carbon dioxide.

Lime is a white, amorphous, infusible substance. When heated in the flame of the compound blow-pipe it gives an intense light, as any other infusible substance would do under the same circumstances. When exposed to the air it attracts moisture and carbon dioxide, and is converted into the carbonate. It must therefore be protected from the air. Lime which has been converted into the carbonate by exposure to the air is said to be *air-slaked*.

**Calcium Hydroxide, Ca(OH)₂.**—When calcium oxide or quick-lime is treated with water it becomes hot and crumbles to a fine powder. The substance which is formed in this operation is somewhat soluble in water, the solution being known as *lime-water*. The chemical change which takes place when lime is treated with water has been explained. It consists in the formation of a compound of the formula $Ca(OH)_2$, known as slaked lime; and the operation is known as *slaking*. The action is of the same kind as that with which we have so frequently had to deal in the transformation of oxides into the corresponding hydroxides. Thus when potassium oxide is treated with water it is changed to the hydroxide, with a marked evolution of heat, the reaction being represented in this way:

$$K_2O + H_2O = \frac{KOH}{KOH}.$$

So, too, when sulphur trioxide is brought in contact with water it appears to form the hydroxide, normal sulphuric acid:

$$S \begin{cases} =O \\ =O \\ =O \end{cases} + 3H_2O = S \begin{cases} OH \\ OH \\ OH \\ OH \\ OH \\ OH \end{cases}.$$

The action in the case of calcium oxide is represented in a similar way:

$$Ca{=}O + H_2O = Ca{<}^{OH}_{OH}.$$

The hydroxide is a fine white powder. At red heat it loses water and is reconverted into the oxide:

$$Ca{<}^{OH}_{OH} = Ca{=}O + H_2O.$$

When lime-water is exposed to the air it becomes covered with a crust of calcium carbonate, and finally all the calcium is precipitated as calcium carbonate. A solution of calcium hydroxide affords a convenient means of detecting the presence of carbon dioxide, as has been shown in dealing with this gas. The solution has an alkaline reaction, and acts in many respects like the hydroxides of potassium and sodium. Attention has been called to the fact that the hydroxides of most of the metals are insoluble in water, and that when a soluble hydroxide is added to the salt of such a metal the insoluble hydroxide is precipitated. The same kind of decomposition of salts is effected by a solution of calcium hydroxide. Thus, when it is added to ferric chloride, ferric hydroxide is thrown down:

$$Fe\begin{cases}Cl\\Cl\\Cl\end{cases}\ \ \ Ca{<}^{OH}_{OH}\qquad Fe\begin{cases}OH\\OH\\OH\end{cases}$$
$$+\ Ca{<}^{OH}_{OH}\ =\qquad\qquad +\ \begin{matrix}CaCl_2\\CaCl_2\\CaCl_2\end{matrix}.$$
$$Fe\begin{cases}Cl\\Cl\\Cl\end{cases}\ \ \ Ca{<}^{OH}_{OH}\qquad Fe\begin{cases}OH\\OH\\OH\end{cases}$$

This reaction is entirely analogous to that which takes place between ferric chloride and potassium hydroxide:

$$Fe\begin{cases}Cl\\Cl\\Cl\end{cases} + \begin{matrix}KOH\\KOH\\KOH\end{matrix} = Fe\begin{cases}OH\\OH\\OH\end{cases} + \begin{matrix}KCl\\KCl\\KCl\end{matrix}.$$

Lime is extensively used in the arts, generally in the form of the hydroxide. As we have seen, it is used in the preparation of ammonia and the caustic alkalies, potassium and sodium hydroxides; and of bleaching-powder and potassium chlorate. It is further used in large quantity in the process of tanning for the purpose of removing the hair from hides; in decomposing fats for the purpose of making stearin for candles; for purifying gas; and especially in the preparation of mortar.

**Bleaching-powder.**—The preparation of bleaching-powder was referred to under Chlorine (which see). The main reaction involved is that represented in the equation

$$2Ca(OH)_2 + 4Cl = \underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Bleaching-powder}} + 2H_2O.$$

The compound is commonly called "chloride of lime." Assuming that the reaction takes place in the same way as that of chlorine on caustic potash, the product is a mixture of calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride, for it is held that the reaction with potassium hydroxide takes place as represented in this equation:

$$2KOH + 2Cl = KClO + KCl + H_2O.$$

An objection to the view that calcium chloride is present as such in bleaching-powder is found in the fact that the substance is not deliquescent, as it should be if calcium chloride were present. This has led to the suggestion that bleaching-powder in the dry form is not a mixture of two compounds, as represented above, but that it is rather one compound of the formula $Ca \begin{cases} Cl \\ OCl \end{cases}$ or $CaOCl_2$. A compound of this formula would plainly have the same composition as a mixture of calcium hypochlorite and calcium chloride in the proportion of their molecular weights. For we have

$$Ca(ClO)_2 + CaCl_2 = 2CaOCl_2.$$

The point is a difficult one to decide, but at present the evidence appears to be rather in favor of the view that bleaching-powder in the dry form is a single compound of the constitution represented by the last formula given. When treated with water, however, it appears to be resolved into a mixture of the hypochlorite and chloride.

Bleaching-powder is a white powder which has the odor of hypochlorous acid. It is soluble in about twenty parts of water, though the commercial product always leaves a slight residue, which consists mainly of calcium hydroxide. When treated with an acid, as sulphuric or hydrochloric acid, it gives up all its chlorine. Thus, with hydrochloric acid the reaction takes place as represented in these equations:

$$Ca(ClO)_2 + 2HCl = CaCl_2 + 2HClO;$$
$$2HCl + 2HClO = 2H_2O + 2Cl_2.$$

With sulphuric acid the action also probably takes place in two stages. The acid acts upon the hypochlorite, setting hypochlorous acid free; and upon the chloride, setting hydrochloric acid free. The hydrochloric and hypochlorous acids then react with each other as represented above:

$$Ca(ClO)_2 + H_2SO_4 = CaSO_4 + 2HClO;$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl;$$
$$2HCl + 2HClO = 2H_2O + 2Cl_2.$$

When exposed to the action of carbon dioxide hypochlorous acid is liberated. Hence, when it is allowed to lie in the air this decomposition takes place slowly. The hypochlorous acid acts further upon the calcium chloride, liberating chlorine:

$$CaCl_2 + 2HOCl + CO_2 = CaCO_3 + H_2O + 2Cl_2.$$

It may be, however, that the action takes place between carbon dioxide and the compound $CaOCl_2$, thus:

$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2.$$

In any case, the fact remains that carbon dioxide sets the chlorine free from bleaching-powder.

A solution of bleaching-powder alone is not capable of bleaching except very slowly. If, however, something is added which has the power to decompose it, bleaching takes place, the action being due to the presence of hypochlorous acid and chlorine. As is clear from what was said above, the passage of carbon dioxide through the solution or the addition of an acid would cause it to bleach. So, too, certain salts produce a similar effect. The explanation of this is the instability of the hypochlorites formed by the salts added. When a concentrated solution of bleaching-powder is heated it gives off oxygen, and the salt is converted into the chloride. In dilute solution, however, the hypochlorite is converted into chlorate and chloride :

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$

This fact is taken advantage of, as has been shown, for the purpose of making calcium chlorate, and from this potassium chlorate (see p. 494). In contact with certain oxides, as copper oxide, ferric oxide, and with hydroxides, as cobalt and nickel hydroxides, a solution of bleaching-powder readily gives up oxygen when heated.

The chief application of bleaching-powder is, as its name implies, for bleaching. It is also used as a disinfectant, and as an antiseptic, that is, for the purpose of destroying disease germs, and of preventing decomposition of organic substances.

**Calcium Carbonate, $CaCO_3$.**—This salt occurs in immense quantities in nature in the well-known forms limestone, calc-spar, marble, and chalk. The variety of calc-spar found in Iceland, and known as Iceland spar, is particularly pure calcium carbonate. It crystallizes in a number of different forms, the most common being in rhombohedrons, as seen in ordinary calc-spar. A second variety of crystallized calcium carbonate is *aragonite*. This is found in nature crystallized in rhombic prisms, and in forms derived from this. When heated

aragonite falls to pieces, the particles being small crystals of the form characteristic of calc-spar. This is a case of dimorphism similar to that presented by sulphur, which, it will be remembered, crystallizes in two forms, the rhombic and monoclinic, the latter of which passes into the former spontaneously. These forms are produced artificially very readily. When calcium carbonate is precipitated from a solution of a calcium salt by adding a soluble carbonate at ordinary temperatures the precipitate is made up of microscopic crystals which have the same form as calc-spar. If, however, the solution from which the carbonate is precipitated is hot, the salt consists of microscopic crystals of the form of aragonite.

The most abundant form of calcium carbonate is limestone, of which many great mountain-ranges are largely made up. This is a compact form of the compound, which has a gray color, and frequently consists of minute crystals. It is always more or less impure, containing clay and other substances. Limestone which is mixed with a considerable proportion of clay is called *marl*. Many natural waters contain calcium carbonate in solution—probably in the form of the acid carbonate. When such a water evaporates the carbonate is again deposited. It happens in some places that a water charged with the carbonate works its way slowly through the earth and drops from the top of a cave. Under these circumstances there is a gradual deposit of the salt which remains suspended. Such hanging formations of the carbonate are known as *stalactites*. At the same time that part of the liquid which falls to the bottom of the cave forms a projecting mass below the stalactite. Such projecting masses are called *stalagmites*. The formation of stalactites takes place in much the same way as that of icicles.

Much of the calcium carbonate found in nature has its origin in the remains of animals, and fossils are very abundant in it. *Chalk* consists almost exclusively of the shells of microscopic animals.

When carbon dioxide is passed into a solution of cal-

cium hydroxide, the carbonate is precipitated ; and, if the current of gas is continued long enough, the carbonate is redissolved. It appears, therefore, that calcium carbonate is soluble in water that contains carbonic acid. It is probable that the cause of this is to be found in the formation of an acid carbonate, possibly the one of the formula HO–OC–O–Ca–O–CO–OH. No positive evidence of the formation of this substance has, however, been furnished. If it is formed, it is certainly very unstable ; for, on heating the solution to boiling, the normal carbonate is precipitated and carbon dioxide is given off. Natural waters which come in contact with limestone gradually take up more or less of the carbonate, with the aid of the carbon dioxide of the air, and when such a water is boiled, the carbonate is thrown down. A water containing calcium carbonate in solution is called a *hard water;* and, as this kind of hardness is easily removed by boiling, it is called *temporary hardness* in order to distinguish it from a kind which is not removed by boiling, and is therefore called *permanent hardness.* Temporary hardness is further removed by adding lime to the water, when normal carbonate is formed, which is at once precipitated.

The decomposition of calcium carbonate by heat, leading to the formation of lime, or calcium oxide, and carbon dioxide, was referred to on p. 468.

**Applications.**—Calcium carbonate is used, in the arts, for a great many purposes, as in the manufacture of glass ; as a flux (see p. 531) in many important metallurgical operations, as in the reduction of iron from its ores ; in the preparation of lime for mortar; etc. As is well known, further, marble and some of the varieties of limestone are extensively used in building ; and large quantities of chalk are also used.

**Calcium Sulphate, $CaSO_4$.**—This compound is very abundant in nature. The principal natural variety is *gypsum*, which occurs in crystals containing two molecules of water, $CaSO_4 + 2H_2O$. This is perhaps derived directly from the normal acid $S(OH)_6$, having the con-

stitution represented by the formula $(HO)_4 S <^O_O> Ca.$
The salt of the formula $CaSO_4$ also occurs in nature, and is called *anhydrite.* A granular form of gypsum is called *alabaster.* Calcium sulphate is difficultly soluble in hot and cold water, but its solubility is markedly increased by the presence of certain other salts ; as, for example, sodium chloride. It is comparatively easily soluble in hydrochloric acid and in nitric acid. When heated to 100°, or a little above, it loses nearly all its water and forms a powder known as *plaster of Paris,* which has the power of taking up water and forming a solid substance. This process of solidification is known as "setting." Plaster of Paris is very largely used in making casts, on account of its power to harden after having been made into a paste with water. The hardening is a chemical process, and is caused by the combination of water with the salt to form the crystallized variety :

$$CaSO_4 + 2H_2O = (HO)_4 S <^O_O> Ca.$$

When heated to 200°, and above, all the water is given off from gypsum, and the product now combines with water only very slowly, and is of no value for making casts. In general, the higher the temperature to which the gypsum is heated, the greater the difficulty with which the product combines with water.

Many natural waters contain gypsum in solution. Such waters act in some respects like those which contain calcium carbonate. With soap, for example, they form insoluble compounds. They are called hard waters. This kind of hardness is not removed by boiling, and it is therefore called *permanent hardness.* Magnesium sulphate acts in the same way, producing permanent hardness.

When calcium sulphate is treated with a solution of a soluble carbonate, it is decomposed, forming the carbonate as represented in the equation

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3.$$

This change is effected simply by allowing the two to stand in contact at the ordinary temperature.

Besides being used for making casts, calcined gypsum is used also in surgery for making plaster-of-Paris bandages, and as a fertilizer. Its action as a fertilizer is believed by some to be due to the fact that it has the power to hold ammonia and ammonium carbonate in combination, and thus to make them available for the plants. It has recently been shown that it in some way facilitates the process of nitrification, and perhaps it is in consequence of this that it facilitates plant-growth.

**Calcium Phosphates.**—There are three phosphates of calcium : (1) The *normal phosphate*, $Ca_3(PO_4)_2$; (2) the *secondary phosphate*, $CaHPO_4$; and (3) the *primary phosphate*, $CaH_4(PO_4)_2$.

(1) *Normal calcium phosphate*, $Ca_3(PO_4)_2$, is derived from phosphoric acid by the replacement of all the hydrogen by calcium. It is found in nature in large quantity as *phosphorite*, and in combination with calcium fluoride or chloride as *apatite*. It is, further, the chief inorganic constituent of bones, forming 85 per cent of bone-ash, and is contained in the excrement of animals, as in guano, etc. It is found everywhere in the soil, and is taken up by the plants for whose development it is essential. That it is also essential to the life of animals is obvious from the fact that the bones consist so largely of it. The phosphate needed for the building up of bones is taken into the system with the food. From these statements, it is clear that calcium phosphate is of fundamental importance, and that a fertile soil must either contain this salt or something from which it can be formed. Now, when a crop is raised on a given area, a certain amount of the phosphate contained in it is withdrawn. If the plants were allowed to decay where they grow, the phosphate would be returned and the soil would continue fertile ; but in cultivated lands this is not the case. The crops are removed, and with them the calcium phosphates contained in them, and the soil therefore becomes exhausted. If the substances removed are used as food, some of the phosphate is found in the excrement of the

animals; and, if this excrement is put on the soil, it is again rendered fertile. There are, however, other sources of calcium phosphate, and some of these are utilized extensively in the preparation of artificial fertilizers. The natural form of the phosphate, as that in bone-ash, in phosphorite, and in guano, is mainly the normal or neutral phosphate. This is insoluble in water, and is therefore taken up by the plants with difficulty. To make it quickly available, it must be converted into a soluble phosphate. This is done by treating it with sulphuric acid in order to effect the reaction represented in this equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The primary phosphate thus formed is soluble in water, and is of great value as a fertilizer. The mixture of the soluble phosphate and of calcium sulphate is known as "superphosphate of lime." The sulphate, as we have seen, is also of value as a fertilizer. The value of superphosphates depends mostly upon the amount of soluble phosphate contained in them; and in dealing with them it is customary to state how much "soluble" and how much "insoluble phosphoric acid" they contain. When a superphosphate is allowed to stand for a time, some of the soluble primary phosphate is converted into insoluble phosphates by contact with basic hydroxides and water. This is known as the process of "reversion," and that part of the phosphoric acid which is contained in the insoluble phosphate is spoken of as "reverted phosphoric acid."

Normal calcium phosphate, as has been stated, is insoluble in water, and is formed when a soluble normal phosphate is added to a solution of a calcium salt. It is also formed when di-sodium phosphate and ammonia are added to a solution of a calcium salt, thus:

$$2HNa_2PO_4 + 3CaCl_2 + 2NH_3 = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl.$$

Di-sodium phosphate alone at first produces a precipitate of the normal phosphate, while the primary phosphate which is formed at the same time remains in solution.

The reaction takes place thus:

$$4HNa_2PO_4 + 4CaCl_2 = CaH_4(PO_4)_2 + Ca_3(PO_4)_2 + 8NaCl.$$

On standing, the primary acts upon the tertiary salt, forming the secondary phosphate thus:

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4HCaPO_4.$$

But even on long standing this reaction is not complete.

Normal or tertiary calcium phosphate is soluble in hydrochloric acid and in nitric acid, in consequence of the formation of calcium chloride, or nitrate, and the primary phosphate. If ammonia is added to this solution, the tertiary phosphate is again precipitated, as represented below:

$$Ca_3(PO_4)_2 + 4HCl = 2CaCl_2 + H_4Ca(PO_4)_2;$$
$$2CaCl_2 + H_4Ca(PO_4)_2 + 4NH_3 = Ca_3(PO_4)_2 + 4NH_4Cl.$$

(2) *Secondary calcium phosphate*, $CaHPO_4$, is formed, as above described, when a solution of a calcium salt is treated with secondary sodium phosphate.

(3) *Primary calcium phosphate*, $H_4Ca(PO_4)_2$, is commonly called the acid phosphate of calcium. It is formed when ordinary insoluble calcium phosphate is treated with concentrated sulphuric acid, and is contained in the so-called superphosphates. It is also formed by treating the neutral phosphate with phosphoric acid and with hydrochloric acid. When treated with but little water, it is converted into the secondary salt and free acid:

$$H_4Ca(PO_4)_2 = HCaPO_4 + H_3PO_4.$$

**Calcium Silicate, $CaSiO_3$,** occurs in nature as the mineral wollastonite, and, in combination with other silicates, in a large number of minerals, as garnet, mica, the zeolites, etc. It is formed when a solution of sodium silicate is added to a solution of calcium chloride, and when a mixture of calcium carbonate and quartz is heated to a high temperature.

**Glass.**—Ordinary glass is a silicate of calcium and sodium made by melting together sand (silicon dioxide, $SiO_2$) with lime and sodium carbonate or soda. In-

stead of calcium carbonate, lead oxide may be used; and instead of sodium carbonate, potassium carbonate. The properties of the glass are dependent upon the materials used in its manufacture.

*Ordinary window glass* is a sodium-calcium glass. The purer the calcium carbonate and silica, the better the quality of the glass. This glass is comparatively easily acted upon by chemical substances, and is therefore not adapted to the preparation of vessels which are to be used to hold acids and other chemically active substances. It answers, however, very well for windows. The difference between ordinary window glass and plate glass is essentially that the former is blown and then cut into pieces, while the latter, when in the molten condition, is run into flat moulds and there allowed to solidify.

*Bohemian glass* is made with potassium carbonate. If pure carbonate is used, as well as pure calcium carbonate and silica, a very beautiful glass is the result. It is characterized by great hardness, by its difficult fusibility, and by its resistance to the action of chemical substances. It is particularly well adapted to the manufacture of vessels and tubes for use in chemical laboratories.

*Flint-glass* is made by melting together lead oxide, potassium carbonate, and silicon dioxide. It is characterized by its power to refract light, its high specific gravity, its low melting-point, and the ease with which it is acted upon by reagents. Owing to its high refractive power, it is largely used in the manufacture of lenses for optical instruments.

*Strass* is a variety of lead-glass which is particularly rich in lead. Its refracting power is so great that it is used in the manufacture of artificial gems.

Colors are given to glass by putting in the fused mass small quantities of various substances. Thus, a cobalt compound makes glass blue; copper and chromium make it green; one of the oxides of copper makes it red; uranium gives it a yellow color; etc. The most common variety of glass is that used in the manufacture of ordinary bottles. It is generally green to black, and sometimes brown. In its manufacture, impure materials are

used, chiefly ordinary sand, limestone, sodium sulphate, common salt, clay, etc.

When glass is suddenly cooled, it is very brittle and breaks into small pieces when scratched or slightly broken in any way. This is shown by the so-called Prince Rupert's drops, which are made by dropping glass, in the molten condition, into water. When the end of such a drop is broken off, the entire mass is completely shattered into minute pieces. It is clear from this that, in the manufacture of glass objects, care must be taken not to cool them suddenly. In fact they are cooled very slowly, the process being known as *annealing*. For this purpose they are placed in furnaces the temperature of which is but little below that of fusion, and they are kept there for some time, the heat being gradually lowered. If red-hot glass is introduced into heated oil or paraffin, and allowed to cool very slowly, it is found to be extremely hard and elastic. The glass of De la Bastie is made in this way. Vessels made of it can be thrown about upon hard objects without breaking, but sometimes a slight scratch will cause the glass to fly in pieces as the Rupert's drops do.

**Mortar.**—Mortar is made of slaked lime and sand. When this mixture is exposed to the air, calcium carbonate is slowly formed and the mass becomes extremely hard. The water contained in the mortar soon passes off, but nevertheless freshly plastered rooms remain moist for a considerable time. This is due to the fact that a reaction is constantly taking place between the carbon dioxide and calcium hydroxide by which calcium carbonate and water are formed,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$

and it is the water thus liberated which keeps the air moist. The complete conversion of the lime into carbonate requires a very long time, because the carbonate which is formed on the surface protects, to some extent, the lime in the interior.

It is generally regarded as unhealthy to live in rooms with freshly plastered walls, because the air is constantly

kept moist in consequence of the reaction above men-
tioned. It is, however, difficult to see why the presence
of a little extra moisture in the air should be unhealthy ;
and, if there is any danger from freshly plastered walls,
it seems probable that the cause must be sought for else-
where. It is possible that the constant presence of
moisture in the pores of the wall interferes with the im-
portant process of diffusion, and that therefore when the
room is closed this natural method of ventilation cannot
come into play.

When lime-stones which contain magnesium carbonate
and aluminium silicate in considerable quantities are
heated for the preparation of lime, the product does
not act with water as calcium oxide does, and this lime
is not adapted to the preparation of ordinary mortar.
On the other hand, it gradually becomes solid, in con-
tact with water, for reasons which are not known. Such
substances are known as *cements*, or *hydraulic cements.*
Other cements besides those made in the manner men-
tioned are known.

**Calcium Sulphide, CaS,** is formed by heating calcium
sulphate with charcoal. It is remarkable on account
of the fact that it is phosphorescent. After having
been exposed to sun-light, it continues to give light for
some time afterward. This and the similar compound,
barium sulphide, are now used quite extensively in the
preparation of luminous objects, such as match-boxes,
clock-faces, plates for house-numbers, etc.

**Calcium Nitride, $Ca_3N_2$,** a brown mass, is formed by
heating a 15–20 per cent amalgam of calcium in dry
atmosphere to dull redness. It is somewhat volatile,
and is decomposed by water, with the formation of cal-
cium hydroxide and ammonia.

**Calcium Carbide, $C_2Ca$,** is formed by heating lime and
carbon together in an electric furnace, when the reac-
tion represented by the following equation takes place :

$$CaO + 3C = C_2Ca + CO.$$

It is manufactured on the large scale, the form of
carbon used being coke. The carbide forms a crystal-

line mass. That of average quality has a reddish color. That of bad quality has a grayish or black color. When pure it is colorless. When treated with water it yields acetylene, $C_2H_2$, a gas that is coming into practical use on account of its value for purposes of illumination (see Acetylene, p. 374).

## STRONTIUM, Sr (At. Wt. 86.95).

**Occurrence and Preparation.**—Strontium occurs in nature in the form of the sulphate, $SrSO_4$, as celestite, and in the form of the carbonate, $SrCO_3$, as strontianite. The latter is found in large quantities in Westphalia. The element is isolated by the action of an electric current on the molten chloride.

**Properties.**—It is very similar to calcium, having a metallic lustre and a brass-yellow color. It is oxidized by contact with the air, and decomposes water rapidly with evolution of hydrogen, which does not, however, take fire spontaneously.

**Compounds of Strontium.**—The compounds of strontium are very similar to those of calcium. Its *chloride* has not the same attraction for water that calcium chloride has, though it deliquesces when left in contact with the air. The *oxide* is not easily made by decomposition of the carbonate by heat, as the carbonate is much more stable than that of calcium. It is, however, prepared without difficulty by heating the nitrate. When brought in contact with water, the oxide forms the *hydroxide*, which is analogous to calcium hydroxide. It is more easily soluble in water than the latter.

*Strontium nitrate*, $Sr(NO_3)_2$, is made in considerable quantity for the purpose of preparing a mixture which, when burned, gives a red light (red-fire, Bengal-fire). It is easily made by dissolving strontianite or strontium carbonate in nitric acid.

*Strontium sulphate*, $SrSO_4$, occurs in nature in beautiful crystals as the mineral celestite. It is formed when a soluble sulphate is added to a solution of a strontium salt. In solubility it lies between calcium sulphate and barium sulphate.

## BARIUM, Ba (At. Wt. 136.39).

**Occurrence and Preparation.**—Barium occurs in nature in the same forms of combination as strontium, viz., as the carbonate, $BaCO_3$, in witherite ; and as the sulphate, $BaSO_4$, in barite or heavy spar. It is prepared by electrolysis of the molten chloride.

**Properties.**—It closely resembles calcium and strontium, being a yellow metal, which is oxidized by contact with the air and readily decomposes water at the ordinary temperature.

**Barium Chloride, $BaCl_2 + 2H_2O$,** is prepared by dissolving barium carbonate in hydrochloric acid. It dissolves easily in water, but not as easily as the chlorides of strontium and calcium. The order of solubility, beginning with the most soluble, is, calcium, strontium, barium,—the same as in the case of the sulphates.

**Barium Hydroxide, $Ba(OH)_2$,** is formed by dissolving barium oxide in water, just as calcium hydroxide is formed by treating calcium oxide with water. In hot water it is much more easily soluble than calcium hydroxide, and it is also more easily soluble in cold water. As such a solution acts in the same general way as lime-water, it is frequently used in the laboratory for the purpose of detecting carbon dioxide, barium carbonate being insoluble. Like lime-water, it has an alkaline reaction.

**Barium Oxide, BaO,** is made by heating the nitrate, as the carbonate is not easily decomposed by heat. The most interesting property of the oxide is its power to take up oxygen when heated to a dark red heat in the air or in oxygen, when it forms

**Barium Peroxide or Dioxide, $BaO_2$.**—This peroxide is a white powder which looks like the simple oxide. When heated to a temperature a little higher than that required for its formation, it breaks down into barium oxide and oxygen. The formation of the peroxide by heating the oxide in the air, and the decomposition of the peroxide at a higher heat, make it possible to extract oxygen from the air and to obtain it in the free state.

This method of preparing oxygen on the large scale from the air was referred to under Oxygen. It is stated that the oxide improves with use. Specimens which have been in use for two years are said to be as efficient as at first. When a solution of hydrogen dioxide, $H_2O_2$, is added to a solution of barium hydroxide, a precipitate is formed which has the composition $BaO_2 + 8H_2O$. When filtered and put in a vacuum over sulphuric acid, it loses all its water and leaves behind pure dioxide. The dioxide is a convenient starting-point in the preparation of hydrogen dioxide. It is only necessary to treat it with hydrochloric acid in order to make a solution of hydrogen dioxide. The solution made in this way, however, contains barium chloride. To make a solution containing nothing but the dioxide, pure barium peroxide is treated with dilute sulphuric acid, when insoluble barium sulphate is formed and the hydrogen dioxide remains in solution :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

It is interesting to compare the action of hydrochloric acid on barium peroxide and on the corresponding compound of manganese. With the latter, as we have seen, the reaction takes place as represented in this equation :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2;$$

while with barium peroxide the reaction takes place thus :

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

It is probable that in the case of manganese dioxide some intermediate reactions take place which are impossible in the other case. (See Manganese Dioxide.)

**Barium Sulphide, BaS,** is made as calcium sulphide is, by reducing the sulphate by heating with charcoal. It is phosphorescent, like the calcium compound. When dissolved in water, it is decomposed, forming the hydrosulphide and hydroxide, thus :

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2.$$

It will be remembered that thermochemical investigations have made it appear probable that similar reactions take place when potassium and sodium sulphides are dissolved in water. In the case of barium sulphide the evidence is more tangible, for, on evaporating a solution of this compound, both the hydrosulphide and hydroxide crystallize out.

**Barium Nitrate, $Ba(NO_3)_2$,** is easily soluble in water, but difficultly soluble in acids, and is precipitated from its solution in water by the addition of nitric acid. When heated to a sufficiently high temperature, it is decomposed, and barium oxide is left behind.

**Barium Sulphate, $BaSO_4$.**—This occurs in nature as barite, or heavy spar, and is precipitated when a soluble sulphate or sulphuric acid is added to a solution of a barium salt. It is insoluble in water; when freshly precipitated, it is easily soluble in concentrated sulphuric acid. It is artificially prepared for use as a pigment and is known as *permanent white*. On account of its insolubility it is much used in chemical analysis for the purpose of detecting and estimating sulphuric acid. It differs markedly from calcium and strontium sulphate, in the fact that, when treated with a solution of ammonium carbonate, it is not converted into the carbonate, whereas calcium and strontium sulphates are by this means completely converted into the carbonates. This fact is taken advantage of in analysis. There are other differences, which will be stated at the end of this chapter.

**Barium Carbonate, $BaCO_3$,** occurs in nature as witherite, and is made pure by adding ammonium carbonate and a little ammonia to a solution of barium chloride. The carbonate usually found in the market is made by precipitating a solution of the crude sulphide with sodium carbonate, or by heating together sodium carbonate and natural barium sulphate, or heavy spar. Made in either of these ways it contains alkaline carbonate, from which it is impossible to separate it by washing. The carbonate, like the other salts of barium, is poisonous. It has the power to unite, and form insoluble compounds, with me-

tallic oxides of the formula $M_2O_3$, as, for example, ferric oxide, $Fe_2O_3$, and is used in analytical operations for the purpose of separating iron from other metals, like manganese, which are not precipitated by it.

**Phosphates of Barium.**—The phosphates of barium correspond in general to those of calcium. When ordinary sodium phosphate and ammonia are added to a solution of a barium salt, normal or tertiary phosphate is precipitated :

$$3BaCl_2 + 2HNa_2PO_4 + 2NH_3 = Ba_3(PO_4)_2 + 4NaCl + 2NH_4Cl.$$

When sodium phosphate alone is added, the first reaction which takes place is that represented in the equation

$$4BaCl_2 + 4HNa_2PO_4 = BaH_4(PO_4)_2 + Ba_3(PO_4)_2 + 8NaCl.$$

The precipitate is the tertiary phosphate, while the primary phosphate is in solution. On standing, the soluble salt acts upon the insoluble one, forming the secondary phosphate thus :

$$BaH_4(PO_4)_2 + Ba_3(PO_4)_2 = 4HBaPO_4.$$

**Reactions which are of Special Value in Analysis.**—The sulphates of calcium and strontium are completely converted into the carbonates by contact with a solution of ammonium carbonate in ammonia. The sulphate of barium is not changed in this way. Consequently, if a mixture of the three sulphates is treated with ammonium carbonate, those of calcium and strontium will be converted into carbonates, while that of barium will remain unchanged. By filtering, washing with water, and treating with dilute nitric or hydrochloric acid, the carbonates will be dissolved, while the sulphate will not. If nitric acid is used, the solution may be evaporated to dryness and treated with a mixture of alcohol and ether. Calcium nitrate will dissolve ; strontium nitrate will not.

*Fluosilicic acid* produces a precipitate of barium fluosilicate, $BaSiF_6$, in solutions of barium salts. This is

insoluble in a mixture of alcohol and water, and difficultly soluble in water. The corresponding salts of calcium and strontium are soluble.

*Calcium sulphate* solution produces a precipitate in a solution of a strontium salt or of a barium salt, but not in one of a calcium salt.

*Strontium sulphate* solution precipitates barium sulphate from a solution of a barium salt, but forms no precipitate in a solution of a strontium salt.

When boiled with a solution of one part of sodium carbonate and three parts of sodium sulphate, the sulphates of strontium and calcium are completely converted into carbonates, while the sulphate of barium remains unchanged.

Barium chloride is insoluble in absolute alcohol; calcium chloride is easily soluble; while strontium chloride dissolves in warm absolute alcohol.

*Ammonium oxalate,* $(NH_4)_2C_2O_4$, produces precipitates of the oxalates in solutions of calcium, barium, and strontium. Only the calcium salt is insoluble in dilute acetic acid.

*Potassium dichromate,* $K_2Cr_2O_7$, precipitates barium chromate, $BaCrO_4$. The corresponding salts of calcium and strontium are soluble in water. Barium chromate is easily soluble in hydrochloric or nitric acid.

All three elements of the group give colored flames which have characteristic spectra. Calcium compounds color the flame reddish yellow; strontium compounds give an intense red; and barium compounds a yellowish green color. The spectra are more complicated than those of the elements of the potassium group, but each one contains highly characteristic lines which are easily recognized.

## MAGNESIUM SUB-GROUP.

### GLUCINUM, Gl (At. Wt. 9.01).

**Occurrence and Preparation.**—The principal form in which the element glucinum occurs in nature is in the mineral beryl, which is a silicate of aluminium and glucinum of the formula $Al_2Gl_3(SiO_3)_6$. Emerald has the

same composition, but is colored green by the presence of a little chromic oxide. The element can be isolated by decomposing the chloride by heating it with potassium or sodium.

**Properties.**—The statements concerning the properties of glucinum, made by those who have prepared it in different ways, differ somewhat from one another, evidently in consequence of the fact that it has not generally been pure. It has a metallic lustre. When heated in the flame of the blow-pipe it becomes covered with a thin layer of oxide, which prevents further action; it dissolves readily in hydrochloric and sulphuric acids, but only with difficulty in nitric acid. It is dissolved by potassium hydroxide, forming in all probability a glucinate of the composition $Gl(OK)_2$:

$$Gl + 2KOH = Gl(OK)_2 + H_2.$$

The specific heat of glucinum at ordinary temperature is 0.425. This multiplied by the atomic weight 9.01 gives 3.83 instead of 6.24. But the analysis and the determination of the specific gravity of the vapor of the chloride show that it has the formula $GlCl_2$, the atomic weight of glucinum being 9.01. At 257° C., however, the specific heat of glucinum is 0.582, and this multiplied by 9.01 gives 5.24. At ordinary temperature, therefore, glucinum, like carbon, boron, and silicon, is an exception to the law of Dulong and Petit, while at a higher temperature, like the elements named, it conforms to the law.

**Compounds of Glucinum.**—The compounds of glucinum differ in many respects from those of the group calcium, barium, strontium. The hydroxide is entirely insoluble in water; the sulphate is easily soluble in water; the chloride is completely decomposed when its water solution is evaporated to dryness, the products being hydrochloric acid and glucinum oxide. It shows a marked tendency to form basic salts.

**Glucinum Chloride**, $GlCl_2$, is formed by the action of chlorine on glucinum, and more easily by treating a mixture of glucinum oxide and carbon with chlorine, the reaction being similar to that employed in making sili-

con chloride (see p. 413) and boron chloride (see p. 352). It is volatile, and it is therefore possible to determine the specific gravity of its vapor. This has been done, with the result of showing its molecular weight to be 79.9. Taking this fact into consideration, together with the percentage composition of the compound, the conclusion is justified that the atomic weight of glucinum is 9.01. For a long time it was thought to be 13.65, with which figure the specific heat, 0.425, is in accordance; for $13.65 \times 0.425 = 5.79$, but the evidence furnished by the specific gravity of the vapor of the chloride is regarded as conclusive in favor of the atomic weight 9.01.

**Glucinum Hydroxide, $Gl(OH)_2$**, is thrown down as a precipitate when a soluble hydroxide is added to a solution of a glucinum salt:

$$GlSO_4 + 2NaOH = Gl(OH)_2 + Na_2SO_4.$$

It is a white, gelatinous mass, which is soluble in potassium and sodium hydroxides and in ammonia, so that, after precipitation from glucinum salts by these reagents, it redissolves. This solution is due to the formation of glucinates of the formula $Gl(OM)_2$:

$$Gl(OH)_2 + 2NaOH = Gl(ONa)_2 + 2H_2O.$$

When sufficiently diluted with water, the potassium and sodium salts are completely decomposed, and the hydroxide reprecipitated. This is an illustration of mass action, a large quantity of water effecting a decomposition which a small quantity does not effect. The power of the hydroxide to form salts with the strong bases shows that it has slight acid properties. The hydroxides of calcium, barium, and strontium do not possess this power.

**Glucinum Sulphate, $GlSO_4$**, is formed by dissolving glucinum hydroxide in dilute sulphuric acid, and has the composition $GlSO_4 + 4H_2O$ when crystallized from water. When a solution of this salt is heated with glucinum hydroxide, basic salts are formed, of which the following are examples: $Gl_2SO_5$ and $Gl_3SO_6$. The first of these is to be regarded as derived from a hydroxide of the formula $HO-Gl-O-Gl-OH$, by neutralization

with sulphuric acid, as represented in the formula $O<_{Gl-O}^{Gl-O}>SO_2$; the second from a hydroxide of the formula HO–Gl–O–Gl–O–Gl–OH, by neutralization with sulphuric acid, as represented in the formula

$$\left. \begin{array}{c} O<_O^{Gl-O} \\ O<_{Gl-O}^{Gl} \end{array} \right\} SO_2.$$

With potassium sulphate, glucinum sulphate forms a double salt of the formula $K_2SO_4 . GlSO_4 + 2H_2O$,

or $\quad \begin{array}{c} SO_2<_O^{OK} \\ SO_2<_{OK}^{O} \end{array}>Gl$, or possibly $\quad \begin{array}{c} (HO)_2SO<_O^{OK} \\ (HO)_2SO<_{OK}^{O} \end{array}>Gl$.

**Glucinum Carbonate, $GlCO_3$.**—When a slight excess of sodium carbonate is added to a solution of glucinum sulphate, a basic carbonate of the formula $Gl_3CO_5$ is formed. This is similar to the second of the above-mentioned basic sulphates. It is to be regarded as derived from the hydroxide HO–Gl–O–Gl–O–Gl–OH by neutralization with carbonic acid, as represented in the formula $\left. \begin{array}{c} O<_O^{Gl-O} \\ O<_{Gl-O}^{Gl} \end{array} \right\} CO$.

**Weak Basic Character of Glucinum.**—The power of glucinum hydroxide to form salts with strong bases, such as potassium and sodium hydroxides, which was referred to above, shows that the hydroxide has slight acid properties. At the same time, as we should expect, its basic properties are weaker than those of the other base-forming elements thus far considered. This is shown in the ready formation of basic salts, such as the basic sulphates and basic carbonates mentioned. The strongest bases do not readily form basic salts, but are, on the other hand, more competent to form stable acid salts. Thus, potassium and sodium form acid carbonates; calcium appears to form an extremely unstable acid carbonate, but preferably all the members of the calcium group form normal carbonates of the general formula $MCO_3$;

glucinum, however, and, as we shall see, magnesium, preferably form basic carbonates. We shall see, further, that the members of the next family, of which aluminium is the principal one, form only extremely unstable compounds with carbonic acid, their basic properties not being sufficiently strong to hold them in combination with the weak acid, except apparently at a very low temperature.

This resemblance to the acid-forming elements is shown by glucinum also by the ease with which its chloride is decomposed into the oxide and hydrochloric acid when its water solution is evaporated to dryness. This reaction does not take place in the case of sodium and potassium at all, nor with barium and strontium. With calcium it takes place to a slight extent, but with glucinum it is complete, as it is with the similar metal magnesium. In general, the more acidic the element the more easily is its chloride decomposed in this way.

## MAGNESIUM, Mg (At. Wt. 24.10).

**Occurrence.**—Magnesium occurs very abundantly in nature, though by no means as abundantly as calcium. Among the widely distributed minerals which contain the element are magnesite, which is the carbonate, $MgCO_3$; dolomite, a double carbonate of magnesium and calcium; serpentine, talc, soapstone, meerschaum, hornblende, all of which contain magnesium silicates. Further, the metal is found in solution in many spring-waters in the form of the sulphate, or, as it is called, Epsom salt. Kainite is a sulphate and chloride of the composition expressed by the formula

$$K_2SO_4.MgSO_4.MgCl_2 + 6H_2O ;$$

kieserite is magnesium sulphate, $MgSO_4 + H_2O$; carnallite is a double chloride, $KMgCl_3 + 6H_2O$.

Magnesium compounds are contained in the soil in consequence of the decomposition of minerals containing it. It is to some extent taken up by the plants, and

subsequently into the animal body. It is found in the bones and in the blood in small quantities.

**Preparation.**—The metal can be made by the electrolysis of its chloride, but is most conveniently made by decomposing the chloride by means of sodium. It is now manufactured in considerable quantity by this method. The operation consists in bringing together dry magnesium chloride, fluor-spar, and sodium in certain proportions, and heating to a high temperature in a crucible. The metal is purified by distillation. Instead of using the chloride, which it is difficult to prepare dry in large quantity, the double chloride of magnesium and potassium, $KMgCl_3$ or $MgCl_2.KCl$, is frequently used.

**Properties.**—It is a silver-white metal with a high lustre. In the air it changes only slowly, but it gradually becomes covered with a layer of the hydroxide. At ordinary temperatures magnesium does not decompose water; at 100° it decomposes it slowly. When heated above its melting-point in oxygen or in the air, it takes fire and burns with a bright flame, forming the white oxide. The light of the flame is very efficient in producing certain chemical changes, such as those involved in photography, when a permanent impression is made by the light upon a sensitive plate. It has also the power to cause hydrogen and chlorine to combine just as the sunlight and the electric light do.

**Applications.**—The principal use to which magnesium is put is for the purpose of producing a bright light, as for photographing in spaces to which the sunlight does not have access, and for signaling. It is also used to some extent as an ingredient of materials employed in making fireworks.

**Compounds of Magnesium.**—The compounds of magnesium present a general resemblance to those of glucinum. As the element is much more abundant in nature, its compounds have been studied more extensively. Its acid properties are somewhat weaker, and its basic properties stronger, than those of glucinum. Its hydroxide does not form salts with the hydroxides of potassium and sodium. On the other hand, its chlo-

ride is decomposed when its water solution is evaporated to dryness. The hydroxide is very slightly soluble in water, and this solution has a slightly alkaline reaction. With carbonic acid it forms basic carbonates similar to those formed by glucinum. On the other hand, it does not readily form basic salts with sulphuric acid. In character, it is plainly more closely allied to the members of the calcium group than glucinum is.

**Magnesium Chloride, MgCl$_2$.**—This salt, as has been stated, occurs in nature. It is easily formed by dissolving magnesium oxide or carbonate in hydrochloric acid. On evaporating at as low a temperature as possible, there finally crystallizes out of the very concentrated solution, a salt of the composition $MgCl_2 + 6H_2O$, analogous to crystallized calcium chloride, $CaCl_2 + 6H_2O$, and strontium chloride, $SrCl_2 + 6H_2O$. When this crystallized salt is heated for the purpose of driving off the water, it is completely decomposed in accordance with the following equation:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

It is most conveniently prepared in the dry form by first making ammonium-magnesium chloride, and decomposing this by heat. For this purpose, a solution of ammonium chloride is added to a solution of magnesium chloride and the whole evaporated to dryness. There is formed in the solution the double salt of the composition $NH_4MgCl_3(MgCl_2.NH_4Cl)$, which can be evaporated to complete dryness. When perfectly dry, this double salt breaks down into magnesium chloride and ammonium chloride, if heated to a sufficiently high temperature. The ammonium chloride under these circumstances is volatilized, and the magnesium chloride remains behind in the molten condition.

The chloride is a white, crystalline mass which deliquesces in the air. At a bright red heat, it is volatile and can be distilled in an atmosphere of hydrogen. It dissolves in water with marked evolution of heat. It combines readily with the chlorides of potassium, so-

dium, and ammonium, forming crystallizing compounds of the formulas $KMgCl_3$, $NaMgCl_3$, and $NH_4MgCl_3$, which may be regarded as formed by the combination of one molecule of magnesium chloride with one molecule of each of the other chlorides. A second compound with potassium chloride, of the formula $K_2MgCl_4$, is also known. It seems probable that the latter is analogous to the potassium compound of glucinum of the formula $Gl <^{OK}_{OK}$. It corresponds to an oxygen compound of the formula, $Mg <^{OK}_{OK}$, which, however, does not seem to be formed. If in this compound we imagine each of the two oxygen atoms to be replaced by two chlorine atoms, the compound would have the formula $Mg <^{(Cl_2)-K}_{(Cl_2)-K}$. The existence of two double chlorides of magnesium and potassium is suggested by what has been said regarding compounds of this kind (see p. 465). One of these would be represented by the formula $Mg <^{Cl}_{(Cl_2)K}$, the other by the above formula. Both are known. Further, magnesium bromide forms the salt $K_2MgBr_4$ or $Mg <^{(Br_2)K}_{(Br_2)K}$.

**Magnesium Oxide, MgO.**—This compound is commonly called *magnesia*. A fine white variety which is known as *magnesia usta*, is made by heating precipitated basic magnesium carbonate. It is a white, loose powder, which is very difficultly soluble in water, forming with it the hydroxide, $Mg(OH)_2$, which is also very difficultly soluble. Magnesia is used, in medicine, as an application to wounds, and, mixed with a solution of ferric sulphate, as an antidote in cases of poisoning by arsenic. As magnesia is infusible, it is used to protect vessels which are subjected to a high temperature. When mixed with water and allowed to lie in the air, it becomes very hard. Mixtures of magnesia with sand also have this property, and are used as hydraulic cements. It is used, further, in the manufacture of fire-bricks.

**Magnesium Sulphate, MgSO₄.**—The mineral kieserite, which occurs in Stassfurt, has the composition expressed by the formula $MgSO_4 + H_2O$; or, more probably, this should be written $(HO)_2MgSO_3$, or $OS\begin{cases} OH \\ OH \\ O \\ O \end{cases}{>}Mg$, in which it appears as a derivative of the acid $SO(OH)_4$. The salt $MgSO_4 + 7H_2O$ (or $H_2MgSO_5 + 6H_2O$), also occurs in nature. It is this variety which is generally obtained when a solution of magnesium sulphate is evaporated to crystallization. It crystallizes in large rhombic prisms, or, if rapidly deposited from very concentrated solutions, in small, needle-shaped crystals. At ordinary temperatures, 100 parts of water dissolve 125 parts of the salt. The water solution has a bitter, salty taste. When heated, it readily loses 6 molecules of water, but it requires a temperature of over 200° to drive off the last molecule. This has led to the belief that the salt with one molecule has the constitution above given, being a derivative of the acid $SO(OH)_4$.

Magnesium sulphate finds extensive application. It is used in medicine as a purgative, and is known as Epsom salt, for the reason that it is contained in the water of Epsom springs; it is used further in the manufacture of sodium sulphate and potassium sulphate, and as a fertilizer in place of gypsum, it having been shown to be advantageous in some cases. Its chief use is for loading cotton fabrics.

Magnesium sulphate forms double salts with other sulphates; as, for example, one with potassium sulphate, similar to that formed by glucinum sulphate (see p. 554). The constitution of the double sulphate of magnesium and potassium is probably that expressed by the formula
$$O_2S{<}\begin{matrix} OK \\ O \end{matrix}{>}Mg.$$
$$O_2S{<}\begin{matrix} O \\ OK \end{matrix}$$

**Magnesium Carbonate, MgCO₃.**— Like glucinum, magnesium shows a marked tendency to form basic salts

with carbonic acid. When a neutral magnesium salt is treated with a soluble carbonate, a basic carbonate is precipitated, the composition of which varies according to the conditions under which it is prepared. The salt obtained by adding an excess of sodium carbonate to a solution of magnesium sulphate has the composition $Mg_3(OH)_2(CO_3)_2$. It is derived from three molecules of magnesium hydroxide and two of carbonic acid, as is more clearly shown in the formula

$$CO <^{O-Mg-OH}_{O} >Mg$$
$$CO <^{O}_{O-Mg-OH}$$

. The salt which is manufactured on the large scale is more complicated than this, being derived from four molecules of magnesium hydroxide and three of carbonic acid. It is known as *magnesia alba*. It is this form of the carbonate which is used in the preparation of *magnesia usta*. Normal magnesium carbonate, $MgCO_3$, occurs in nature as magnesite. It crystallizes in the same form as calcium carbonate, or is isomorphous with it. It is insoluble in water, but like calcium carbonate it dissolves in water containing carbon dioxide in solution. From this solution crystals having the composition $MgCO_3 + 3H_2O$ and $MgCO_3 + 5H_2O$ are deposited under the proper conditions.

**Phosphates.**—The conduct of the phosphates of magnesium is very similar to that of the phosphates of calcium. All three are known; and of these only the primary salt is soluble in water. A salt much utilized in analysis is *ammonium-magnesium phosphate*, $Mg(NH_4)PO_4$. This is difficultly soluble in water, and may therefore be used either for the purpose of detecting magnesium or phosphoric acid. In order to produce this salt, ammonia and some ammonium salt, together with a soluble magnesium salt, must be added to a soluble phosphate. If ammonia alone were added to a solution containing a magnesium salt, magnesium hydroxide would be precipitated:

$$MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4.$$

With ammonium salts, however, magnesium salts form compounds, which are not decomposed on the addition of ammonia. When a soluble phosphate is added, the difficultly soluble ammonium-magnesium salt is thrown down. When heated, this salt loses ammonia, then water, and is converted into magnesium pyrophosphate:

$$Mg(NH_4)PO_4 = MgHPO_4 + NH_3;$$
$$2MgHPO_4 = Mg_2P_2O_7 + H_2O.$$

The corresponding salt of arsenic acid, $Mg(NH_4)AsO_4$, is very similar to the phosphate, and on account of its insolubility it is also used in chemical analysis.

**Borates.**—A borate of magnesium together with magnesium chloride occurs in nature, and is known as boracite. It has the composition expressed by the formula $2Mg_3B_8O_{15} + MgCl_2$. The borate, $Mg_3B_8O_{15}$, is derived from the acid, $H_6B_8O_{15}$, which is related to normal boric acid, as is shown by the equation

$$8B(OH)_3 = H_6B_8O_{15} + 9H_2O.$$

**Silicates.**—The simplest silicate of magnesium found in nature is olivine, which is represented by the formula $Mg_2SiO_4$. It is the neutral salt of normal silicic acid. Serpentine is derived from the acid, $O < \frac{Si(OH)_3}{Si(OH)_3}$, and has the composition $Mg_3Si_2O_7 + 2H_2O$.

**Magnesium Silicide, Mg₂Si,** is made by heating together magnesium chloride, sodium fluosilicate, sodium chloride, and sodium. Under these circumstances the sodium sets magnesium free from the chloride, and silicon from the fluosilicate. Both unite to form magnesium silicide. When treated with hydrochloric acid it gives silicon hydride, $SiH_4$, and hydrogen:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

The liberation of hydrogen is due to the presence of an excess of magnesium.

**Reactions of Magnesium Salts which are of Special**

**Value in Chemical Analysis.**—*Soluble hydroxides* (KOH, NaOH, NH₄OH) precipitate magnesium hydroxide. If ammonium chloride is present ammonia does not precipitate the hydroxide.

*Di-sodium phosphate* with ammonia and ammonium chloride precipitates ammonium-magnesium phosphate from the solution of a magnesium salt.

*Sodium* and *potassium carbonates* precipitate basic magnesium carbonate.

## ERBIUM, E (At. Wt. 165.06).

**General.**—As regards the position of erbium in the periodic system, a final statement cannot as yet be made. According to its atomic weight, assuming it to be 165.06, it falls in the second family. On the other hand, the composition of its compounds seems to indicate rather that it belongs in the third family, as it resembles aluminium in some respects. It occurs in some rare minerals, as cerite, gadolinite, euxenite, and orthite, which are found in Sweden and Greenland. It is always accompanied by other rare metals, a few of which have been studied with care. Among these may be mentioned lanthanum, cerium, didymium, and scandium. These metals will be treated of in later chapters. It need only be said further in regard to erbium, that our knowledge concerning it is as yet quite imperfect, and the cause of this is to be found in the fact that the minerals in which it occurs are exceedingly complex, and it is therefore very difficult to separate the various metals present. It appears that the formula of the oxide of erbium is $E_2O_3$. If this is so, it is in this respect like aluminium oxide, $Al_2O_3$.

It appears probable that the oxide of erbium that is generally obtained from the complex minerals named is a mixture of oxides of rare elements. There is good evidence of the presence of *thulium* and of *holmium*, though it is still an open question whether these as well as erbium may not be capable of further decomposition.

# CHAPTER XXVII.

### ELEMENTS OF FAMILY III. GROUP A :
### ALUMINIUM—SCANDIUM—YTTRIUM—YTTERBIUM—
### SAMARIUM—HELIUM.

**General.**—There is in some respects a resemblance between boron and the principal member of this group ; but as boron acts almost exclusively as an acid-forming element, it was taken up in connection with the elements of Family V, Group B, or the nitrogen group. Attention was, however, called to the fact that the analogy between these elements and boron is but slight. The points of resemblance between boron and the members of Family III, Group A, will be pointed out below. The principal member of this group is aluminium. The others are all rare, and some have been but imperfectly studied, owing to serious difficulties in the way of obtaining their compounds in pure condition. They are trivalent in their compounds, the general formulas being such as the following :

$$MCl_3, \; M(OH)_3, \; M(NO_3)_3, \; M_2(SO_4)_3, \; M_2(CO_3)_3, \; MPO_4, \text{ etc.}$$

Aluminium oxide is weakly basic, and somewhat acidic, though less so than boron. Aluminium hydroxide has the power to neutralize most acids, and also to form salts with strong bases. Boron oxide, on the other hand, has scarcely any basic properties, though it does form a few extremely stable compounds, in which the boron replaces the hydrogen of acids. (See Boron Phosphate, p. 356.)

### Aluminium, Al (At. Wt. 26.91).

**Occurrence.**—Aluminium is an extremely important element in nature and in the arts. It occurs very

widely distributed, and very abundantly in many different forms of combination. Among them are feldspar, mica, cryolite, bauxite. Feldspar is a silicate of aluminium and potassium of the formula $AlKSi_3O_8$. Mica is a general name applied to a large number of minerals which are silicates of aluminium and some other metal, as potassium, lithium, magnesium, etc. The simplest form of mica is that represented by the general formula $KAlSiO_4$, according to which the mineral is a salt of orthosilicic acid, $Si(OH)_4$. Cryolite is a double fluoride of aluminium and sodium, or the sodium salt of fluoaluminic acid, $Na_3AlF_6$. Bauxite is a hydroxide of aluminium in combination with a hydroxide of iron. Besides in the above forms, aluminium occurs in the products of decomposition of minerals. One of the most important of these is clay, which is found in all conditions of purity—from the white kaoline to ordinary dark-colored clay. Kaoline is the aluminium salt of orthosilicic acid of the formula $Al_4(SiO_4)_3 + 4H_2O$. Aluminium silicate is found in all soils, but is not taken up by plants, and does not find entrance into the animal body. The name aluminium has its origin in the fact that the salt alum was known at an early date, and the metal was afterwards isolated from it.

**Preparation.**—The preparation of aluminium on the large scale presents a problem of the highest importance to the human race. The element has properties which adapt it to many uses to which iron is put, and for many purposes it has many advantages over iron. Further, we are supplied by nature with unlimited quantities of the compounds of aluminium, which are distributed everywhere over the earth. While, however, iron, lead, tin, copper, and other metals can be isolated from their natural compounds without serious difficulty, aluminium, which is more abundant than any of them, and in many respects more valuable than any of them, is locked in its compounds so firmly, that it is only by comparatively complicated and expensive methods that it can be isolated ; and up to the present it cannot be made at a price sufficiently low to bring it into common use. At

the same time work is constantly in progress with reference to this important practical problem, and it seems probable that through a thorough study of the laws of chemistry some method for the cheap preparation of aluminium on the large scale will eventually be discovered.

The first method devised for the preparation of aluminium on the large scale consisted in heating aluminium chloride with sodium. The chloride was heated to boiling in a retort; the vapor passed through a vessel containing pieces of iron heated to redness, and then into a long tube containing sodium. Instead of aluminium chloride, the double chloride of aluminium and sodium, which is more easily prepared in the dry condition, is now used. The double chloride and cryolite are heated together with sodium in a properly constructed furnace. It is, further, possible to prepare aluminium by electrolysis of the chloride or of the double chloride above mentioned; and the oxide can be reduced by mixing it with charcoal and passing the current from a powerful dynamo-machine through it. By the latter method an alloy of aluminium and copper is now prepared, but the preparation of aluminium alone by this method does not appear to be entirely successful. New methods for the preparation of the metal are constantly being devised, and the price is constantly being lowered. The latest method of promise consists in the electrolysis of aluminium oxide, in the form of corundum, in a bath of molten cryolite contained in a carbon crucible. A large number of patents have been issued, covering methods for the preparation of aluminium; but these are frequently so imperfectly described, and the evidence of their value so unsatisfactory, that it is difficult to pass judgment upon them. Until recently the commercial preparation of aluminium has appeared to be intimately connected with that of the commercial preparation of sodium; but, in view of the success of the electrolytic method, this is no longer the case.

**Properties.**—The color of aluminium is like that of tin, and it has a high lustre. It is very strong, and yet malleable. It is lighter than most metals in common use,

its specific gravity being 2.5 to 2.7 according to the condition, while that of iron is 7.8, that of silver 10.57, that of tin 7.3, and that of lead 11.37. It does not change in dry or in moist air; and in the compact form it does not act upon water even at elevated temperatures. It melts at about 700°, which is higher than the melting-point of zinc, and lower than that of silver. Hydrochloric acid dissolves it with ease, forming aluminium chloride. At the ordinary temperatures nitric and sulphuric acids do not act upon it; at higher temperatures, however, action takes place, and the corresponding salts are formed. It dissolves in solutions of the caustic alkalies, forming the so-called aluminates. It reduces many oxides when heated with them to a sufficiently high temperature; and is used in the preparation of boron and silicon.

**Applications.**—The metal is used to a considerable extent in the preparation of ornaments, and of useful articles in which lightness is a matter of importance, as in telescopes and opera-glasses. An alloy with a small percentage of silver is used for the beams of chemical balances. Aluminium bronze, which is an alloy with copper, is also used quite extensively. It will be again referred to under Copper.

**Aluminium Chloride, $AlCl_3$.**—When aluminium hydroxide is dissolved in hydrochloric acid a solution of aluminium chloride is formed, and from this solution a compound of the formula $AlCl_3 + 6H_2O$ can be obtained in crystallized form. Like calcium and magnesium chlorides, this salt is deliquescent. When heated to drive off the water the salt conducts itself like magnesium chloride, but the decomposition into the oxide and hydrochloric acid takes place more easily than that of magnesium chloride. The reaction is represented by the equation

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl.$$

The dry chloride is prepared by the same method as that used in the preparation of silicon chloride and boron chloride, viz., by passing chlorine over a heated mixture of the oxide and carbon. The chloride, being volatile,

sublimes, and is deposited in the cool part of the vessel, when pure, as a white laminated crystalline mass. Generally, however, it is more or less colored in consequence of the presence of impurities. When exposed to the air it attracts moisture and gives off hydrochloric acid. It dissolves in water very easily, with a marked evolution of heat, but, from what was said above, it is evident that it cannot be obtained from this solution again by evaporation. It is volatile without change. The specific gravity of its vapor has been determined by different observers, and, unfortunately, with different results. According to Deville and Troost, it is such as to lead to the formula $Al_2Cl_6$. Quite recently, however, Nilson and Pettersson have found it to correspond to that required by the formula $AlCl_3$, their determinations having been made at a higher temperature than those of Deville and Troost. Still later determinations by Crafts again lead to the formula $Al_2Cl_6$. Upon the basis of the determinations by Deville and Troost, chemists have for some time past used the formula $Al_2Cl_6$ to represent the compound. According to this, aluminium would appear to be quadrivalent, as represented in the following formula for the chloride:

$$\begin{array}{c} Cl \\ Cl \end{array}\!\!\!>\!Al\!-\!Al\!<\!\!\!\begin{array}{c} Cl \\ Cl \end{array}$$ . On the other hand, in a compound

made by replacing the chlorine of this chloride by certain organic groups the aluminium appears to be trivalent, as represented in the formula $Al(CH_3)_3$, in which the group $CH_3$, known as methyl, is univalent. Further, the position of aluminium in the periodic system makes it appear extremely probable that it is trivalent, and not quadrivalent. What, then, is the explanation of the discrepancy above noted in the evidence regarding the constitution of the chloride? When we come to examine the conduct of aluminium chloride towards the chlorides of other metals, and find with what ease it forms double chlorides, it seems not improbable that aluminium chloride itself, at ordinary temperatures, and even in the form of vapor at lower temperatures, may be a compound of the same order as the double chlorides. It has been suggested

that in these compounds chlorine is probably in combination with chlorine, as fluorine is with fluorine in hydrofluoric acid, in such a way that two chlorine atoms can exert a linking function between two other atoms. Just as there is a compound of the formula $Al\underset{\diagdown(Cl_2)K}{\overset{\diagup Cl}{-Cl}}$ , so it is possible that aluminium chloride may have the constitution represented by the formula $Al\underset{\diagdown(Cl_2)}{\overset{\diagup(Cl_2)}{-(Cl_2)-}}Al$, in which the aluminium is trivalent. By replacing the chlorine in a compound of this constitution by groups like methyl, which cannot exert the linking function, the product would not be a double compound. Further, by heating a compound of this constitution it would probably dissociate into two molecules of the simple compound $AlCl_3$, and it would be this which comes into play in chemical reactions. In view of the conflicting state of the evidence and the plausibility of the above explanation, the formula for aluminium chloride used here is the simpler one. By means of it and similar formulas for the other compounds of aluminium, the reactions of the element can be expressed somewhat more easily and probably just as truthfully as by means of the more complicated formula.

**Chloroaluminates or Double Chlorides of Aluminium and Analogous Compounds.**—These compounds have been repeatedly referred to, and but very little need be added to what has already been said concerning them. In general, the chloride, bromide, and iodide of aluminium combine with the chlorides, bromides, and iodides of the most strongly marked metals, such as potassium and sodium. Those with potassium and sodium have the formulas $AlCl_3.KCl$ and $AlCl_3.NaCl$, or probably $Al\underset{\diagdown(Cl_2)K}{\overset{\diagup Cl}{-Cl}}$ and $Al\underset{\diagdown(Cl_2)Na}{\overset{\diagup Cl}{-Cl}}$ . The fluoride forms two compounds with potassium fluoride and two with sodium fluoride.

These have the composition represented by the formulas $AlF_3.2KF$, $AlF_3.2NaF$, and $AlF_3.3KF$, $AlF_3.3NaF$, and the constitution expressed thus, $Al{\Large\langle}{\overset{\displaystyle F}{\underset{(F_2)K}{(F_2)K}}}$ and

$Al{\Large\langle}{\overset{(F_2)K}{\underset{(F_2)K}{(F_2)K}}}$ . The tri-sodium fluoaluminate is the mineral cryolite, which occurs in such large quantity as to be exported, and form the starting-point in the preparation of aluminium and even sodium compounds. A method for making sodium carbonate from cryolite has already been described. Its use in the preparation of aluminium compounds will be taken up as far as may be necessary in this chapter.

Besides the compounds with metallic chlorides, aluminium chloride also forms compounds with the chlorides of the acid-forming elements. Such, for example, are the compounds with sulphur tetrachloride and with phosphorus pentachloride. These have the composition represented by the formulas $(AlCl_3)_2SCl_4$ and $AlCl_3.PCl_5$. The latter may be the chlorine analogue of aluminium phosphate, $AlPO_4$. If the oxygen in the phosphate should be replaced by an equivalent quantity of chlorine the result would be a compound of the formula $AlPCl_8$, which is that of the above compound. These double chlorides, like the chlorides of the acid-forming elements in general, are easily decomposed by water, yielding the corresponding oxygen compounds. A compound intermediate between the oxygen and the chlorine compounds is that formed by the combination of aluminium chloride with phosphorus oxychloride, which is represented by the formula $AlPOCl_6$, or $AlCl_3.POCl_3$. This may be regarded as aluminium phosphate, in which three of the oxygen atoms have been replaced by six chlorine atoms.

**Aluminium Hydroxide, $Al(OH)_3$.—** Normal aluminium hydroxide, $Al(OH)_3$, occurs in nature as the mineral hydrargillite. It is precipitated from a solution of aluminium chloride by ammonia:

$$AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl.$$

Obtained by precipitation it forms a gelatinous mass, which is suggestive of starch-paste, and it is on this account extremely difficult to wash it completely free from the substances in the solution. It dries in the air, forming a gummy substance which has the composition $Al(OH)_3$. When heated under proper conditions it loses water, and forms the compound $AlO_2H$ :

$$Al(OH)_3 = AlO.OH + H_2O.$$

This compound is found in nature as the mineral diaspore. If heated to a higher temperature it is converted into the oxide, $Al_2O_3$ :

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

In the conduct of the chloride and of the hydroxide aluminium exhibits a certain resemblance to boron. The acidic character of the latter is, however, more strongly marked than that of the former. Boron chloride is more easily decomposed by water than aluminium chloride, and, as the decomposition takes place at the ordinary temperature, the product is the hydroxide instead of the oxide, as in the case of aluminium. The hydroxide, $B(OH)_3$, readily loses water and forms metaboric acid, which in composition is analogous to diaspore ; and at a higher temperature the oxide, $B_2O_3$, is formed.

Besides the normal hydroxide, $Al(OH)_3$, and that of the formula $AlO(OH)$, there is a third one known. This has the composition $Al_2O(OH)_4$, and, as is plain, is derived from two molecules of the normal hydroxide by loss of one molecule of water :

$$2Al{<}^{OH}_{OH}{>}_{OH} = {}^{HO}_{HO}{>}Al\text{--}O\text{--}Al{<}^{OH}_{OH} + H_2O.$$

This has been obtained in solution ; or, rather, it has been obtained by evaporation of a solution of hydroxide made by continued boiling of a solution of basic acetate of aluminium which decomposes into hydroxide and acetic acid, the latter then evaporating. From this solution, by evaporation in a water-bath, the above hy-

droxide is obtained. As already stated, bauxite is, in all probability, a compound of this constitution combined with a similar hydroxide of iron. A hydroxide of the same composition is obtained when a solution of the normal hydroxide in caustic soda is boiled with ammonium chloride. The precipitate formed in this way is not gelatinous, and, when dried, it has the composition $Al_2O(OH)_4$.

The preparation of aluminium hydroxide from natural compounds of the element is based upon the fact that aluminium oxide forms with sodium a soluble compound, and that this is decomposed by carbon dioxide with precipitation of the hydroxide. The sodium compound formed has probably the composition $Al(ONa)_3$, being a salt of the normal hydroxide. When this is treated in solution with carbon dioxide, the decomposition takes place as represented in this equation:

$$2Al(ONa)_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2Al(OH)_3.$$

When cryolite is ignited with lime, the products are probably calcium fluoride, sodium oxide, and another variety of sodium aluminate:

$$Na_3AlF_6 + 3CaO = NaAlO_2 + Na_2O + 3CaF_2.$$

When the mass is treated with water, the calcium fluoride remains undissolved, while the sodium and aluminium form the compound $Al(ONa)_3$. This undergoes decomposition, as above represented, when treated with carbon dioxide. Two valuable products—aluminium hydroxide and sodium carbonate—are thus obtained.

In order to prepare the hydroxide from bauxite, this is heated to a high temperature with sodium carbonate. Water extracts sodium aluminate, from which the hydroxide is precipitated by means of carbon dioxide.

Aluminium hydroxide forms the material for the preparation of aluminium salts; as, the chloride, sulphate, alum, etc.

**Aluminates.**—When sodium or potassium hydroxide is added to a solution of an aluminium salt, aluminium hydroxide is at first precipitated, but an excess of the re-

agent used dissolves the precipitate. This action is the same in character as that which takes place in the case of glucinum, and is due to the acidic character of aluminium hydroxide. It is probable that in solution the action with potassium and sodium hydroxides is of the same kind as represented in the equations

$$\text{Al(OH)}_3 + 3\text{KOH} = \text{Al(OK)}_3 + 3\text{H}_2\text{O, and}$$
$$\text{Al(OH)}_3 + 3\text{NaOH} = \text{Al(ONa)}_3 + 3\text{H}_2\text{O.}$$

On evaporating the solution of the potassium salt, however, the product obtained has the formula AlO.OK, and is plainly the salt of the hydroxide AlO.OH, which may be called meta-aluminic acid, to suggest its analogy to metaboric acid, BO.OH. When aluminium hydroxide and sodium carbonate are melted together, the salt AlO.ONa is formed, as has been shown by determining the amount of carbon dioxide given off when a known weight of the hydroxide is employed. When, however, the solution of the hydroxide in caustic soda is evaporated, the salt Al(ONa)₃ is deposited.

These salts are very unstable, though their solutions can be boiled without undergoing decomposition. Carbon dioxide decomposes them at once with precipitation of aluminium hydroxide, as was stated in describing the method for the preparation of the hydroxide from cryolite and from bauxite. Similar salts are formed with calcium and barium. Among them may be mentioned those of the following formulas: $\text{Ca}_3(\text{AlO}_3)_2$, $\text{Ca}(\text{AlO}_2)_2$, $\text{Ba}_3(\text{AlO}_3)_2$, and $\text{Ba}(\text{AlO}_2)_2$. The calcium salts are insoluble in water, and some of them become hard in contact with water. They are therefore of importance in the manufacture of hydraulic cements. The barium salts are soluble in water.

Many aluminates occur in nature, forming the important group of minerals known as the *spinels*. Of these, spinel itself is the magnesium salt of the hydroxide AlO.OH, and is represented by the formula $\dfrac{\text{AlO.O}}{\text{AlO.O}} > \text{Mg}$, or $\text{Mg(AlO}_2)_2$. Chrysoberyl is the corresponding glucinum salt $\text{Gl(AlO}_2)_2$; and gahnite is the zinc salt $\text{Zn(AlO}_2)_2$. These salts are extremely stable, differing markedly in this

respect from those above referred to, which are made in the laboratory. They are decomposed by heating them, in finely powdered condition, with primary or acid potassium sulphate, the action of which was described on p. 499. As will be seen farther on, there are other salts similar to the aluminates in structure which occur in nature. Among these there may be mentioned here chromic iron, or chromite, which is an iron salt of a hydroxide of chromium of the formula $CrO.OH$. The salt is to be regarded as made up according to the formula $\frac{CrO.O}{CrO.O} > Fe$, or $Fe(CrO_2)_2$. Further, magnetic oxide of iron or magnetite, $Fe_3O_4$, is regarded as belonging to the same group, and its constitution represented thus: $\frac{FeO.O}{FeO.O} > Fe$, or $Fe(FeO_2)_2$; and there is also a compound of magnesium, $\frac{FeO.O}{FeO.O} > Mg$. For the sake of emphasizing these analogies, the formulas of the compounds above mentioned are here presented in tabular form:

| | | |
|---|---|---|
| Potassium aluminate, | . . | $AlO.OK$ |
| Sodium aluminate, | . . . | $AlO.ONa$ |
| Calcium aluminate, | . . . | $\frac{AlO.O}{AlO.O} > Ca$ |
| Barium aluminate, | . . . | $\frac{AlO.O}{AlO.O} > Ba$ |
| Spinel, | . . . . . . . | $\frac{AlO.O}{AlO.O} > Mg$ |
| Chrysoberyll, | . . . . . | $\frac{AlO.O}{AlO.O} > Gl$ |
| Gahnite, | . . . . . . | $\frac{AlO.O}{AlO.O} > Zn$ |
| Chromite, | . . . . . . | $\frac{CrO.O}{CrO.O} > Fe$ |
| Magnetite, | . . . . . . | $\frac{FeO.O}{FeO.O} > Fe$ |
| Magnesio-ferrite, | . . . . | $\frac{FeO.O}{FeO.O} > Mg.$ |

There is a highly instructive analogy between the aluminates and the double chlorides and other similar

compounds. In general, aluminium hydroxide acts upon the hydroxides of the strongest base-forming elements to form aluminates. So, also, aluminium chloride acts upon the chlorides of the strongest base-forming elements to form double chlorides. By melting together aluminium hydroxide and potassium or sodium hydroxide, compounds of the formulas AlO.OK and AlO.ONa are formed. So, also, by melting together aluminium chloride and potassium or sodium chloride, compounds of the formulas $AlCl_4K$ and $AlCl_4Na$ are formed. Comparing these oxygen and chlorine compounds, it is clear that they are analogous. If the oxygen of the former is replaced by an equivalent quantity of chlorine, the chlorine compounds result:

$$KAlO_2 \qquad KAlCl_4$$
$$NaAlO_2 \qquad NaAlCl_4$$

Or, if their constitutional formulas are written in accordance with the views already expressed regarding the double chlorides, the analogy is also seen, thus:

$$Al{<}^{O}_{OK} \qquad Al{<}^{Cl}_{\substack{Cl \\ (Cl_2)K}}$$

$$Al{<}^{O}_{ONa} \qquad Al{<}^{Cl}_{\substack{Cl \\ (Cl_2)Na}}.$$

The compounds of the same order as cryolite have their analogues in such oxygen compounds as $Al(ONa)_3$, etc., as is shown by the following formulas:

$$Na_3AlO_3 ; \qquad Na_3AlF_6 ;$$

$$Al{<}^{ONa}_{\substack{ONa \\ ONa}} ; \qquad Al{<}^{(F_2)Na}_{\substack{(F_2)Na \\ (F_2)Na}}.$$

It is not improbable that by fusion with other chlorides besides those of potassium and sodium, aluminium chloride will be found to yield other double chlorides analogous to the spinels. According to what was said in

discussing the subject of double chlorides in general, three series of such salts may be looked for, corresponding to the formulas

$$Al \big\langle \begin{matrix} Cl \\ Cl \\ (Cl_2)M \end{matrix}, \qquad Al \big\langle \begin{matrix} Cl \\ (Cl_2)M \\ (Cl_2)M \end{matrix}, \quad \text{and} \quad Al \big\langle \begin{matrix} (Cl_2)M \\ (Cl_2)M \\ (Cl_2)M \end{matrix} ;$$

and representatives of all these classes are known. Oxygen compounds corresponding to the first and last of these have been mentioned. As an example of an oxygen compound corresponding to the second one, barium aluminate, of the formula $Ba_2Al_2O_5$, may be cited.

**Aluminium Oxide, $Al_2O_3$.**—As has been stated, the oxide is formed by heating the hydroxide. It is found in nature in the form of ruby, sapphire, and corundum. The natural variety is extremely hard; and granular corundum, which is known as *emery*, is used for polishing. The red color of the ruby is caused by the presence of a trace of a chromium compound; while the blue color of the sapphire is probably due to the presence of a trace of a cobalt compound. Aluminium oxide is infusible in the hottest furnace fire, but it melts in the flame of the oxyhydrogen blow-pipe, and on cooling it becomes crystalline. By mixing it with various easily fusible substances and heating, it is obtained in the form of crystals, and by adding certain metallic oxides these crystals can be colored. In this way artificial rubies and sapphires have been prepared, which have all the properties of the natural ones. When the oxide is moistened with a few drops of a solution of cobaltous nitrate and then ignited, it turns blue. This fact is taken advantage of in chemical analysis for the purpose of detecting aluminium. When the oxide is made by gently igniting the hydroxide, it dissolves in strong acids. If, however, it is heated to a high temperature, acids will not dissolve it. The natural varieties of the oxide, further, are not soluble in acids. By fusion with acid potassium sulphate insoluble aluminium oxide is converted into a soluble compound.

**Aluminium Sulphate, $Al_2(SO_4)_3$.**—This salt is made by dissolving the hydroxide of aluminium in dilute sulphuric acid, and evaporating to crystallization, when a salt of the composition $Al_2(SO_4)_3 + 18H_2O$ is deposited. When heated the salt loses its water of crystallization, and, if the temperature is raised to that of red heat, the anhydrous salt is decomposed with loss of sulphur trioxide and formation of aluminium oxide. This decomposition is, however, not complete. The sulphate is manufactured on the large scale for various purposes, as, for example, for a mordant, for sizing paper, etc.

**Basic Aluminium Sulphates.**—A solution of ordinary aluminium sulphate has an acid reaction, and has the power to dissolve metals, such as zinc, and hydroxides, such as aluminium hydroxide. When a solution of the sulphate is treated with the hydroxide, a basic salt of the formula $Al_2O(SO_4)_2 + H_2O$ is formed. This should probably be represented by the formula $Al \begin{cases} O \\ O \\ OH \end{cases} >SO_2$ or $Al(OH)SO_4$. Another basic salt has the formula $(AlO)_2SO_4$, the salt being derived from the hydroxide, $AlO.OH$, as represented thus: $\dfrac{AlO.O}{AlO.O} >SO_2$. The former salt is soluble in water. When, therefore, a solution of sodium or ammonium carbonate is added to a solution of ordinary aluminium sulphate, the first portions of hydroxide which are precipitated redissolve in the excess of the ordinary salt. There are other basic salts, some of which occur in nature.

**Alums.**—When a solution of aluminium sulphate is brought together with a solution of potassium sulphate in the proportion of their molecular weights, a salt crystallizes out which has the composition represented by the formula

$$KAl(SO_4)_2 + 12H_2O \quad \text{or} \quad K_2SO_4 + Al_2(SO_4)_3 + 24H_2O.$$

The most rational view which has been expressed regarding this compound is that it has the constitution

$$SO_2 \left< \begin{matrix} OK \\ O \end{matrix} \right.$$
$$SO_2 \left< \begin{matrix} O \\ O \end{matrix} \right> Al,$$ with perhaps some of the so-called water

of crystallization present in the form of hydroxyl. This salt, which has long been known under the name of *alum*, is the type of a class of similar compounds, all of which are called alums. These alums may be regarded as derived from the ordinary form by replacing the potassium by sodium, ammonium, or any other member of the sodium group, besides some other metals. Thus a series of alums is obtained, of which the following are examples:

$$NaAl(SO_4)_2 \quad + 12H_2O \; ;$$
$$LiAl(SO_4)_2 \quad + 12H_2O \; ;$$
$$(NH_4)Al(SO_4)_2 + 12H_2O \; ;$$
$$CsAl(SO_4)_2 \quad + 12H_2O \; ;$$
$$TlAl(SO_4)_2 \quad + 12H_2O.$$

Again, alums are derived from the ordinary form by replacing the aluminium by some other elements which have the power to form compounds resembling those of aluminium, as, for example, iron, chromium, and manganese. Such alums are those represented by the following formulas:

$$KFe(SO_4)_2 + 12H_2O \; ;$$
$$KCr(SO_4)_2 + 12H_2O \; ;$$
$$KMn(SO_4)_2 + 12H_2O.$$

In each of these, again, the potassium can be replaced as in the case of ordinary alum; so that the class includes a comparatively large number of salts. All have certain properties in common. They are all soluble in water, and all crystallize in the same forms, which are regular octahedrons combined with cubes. If a crystal of one alum be suspended in the solution of any other one it will continue to grow. They are all strictly isomorphous. The principal alums containing aluminium are those of

potassium and ammonium, both of which are manufactured on the large scale.

**Potassium Alum, Potassium - Aluminium Sulphate, KAl(SO₄)₂ + 12H₂O.**—Ordinary alum is found in nature in some volcanic regions. The mineral alunite, which is a basic salt of the formula $K(AlO)_3(SO_4)_2 + 3H_2O$, or perhaps $K[Al(OH)_2]_3(SO_4)_2$, occurs in larger quantities. When this salt is heated and treated with water, ordinary alum dissolves, and is easily obtained from the solution. Another source of alum is *alum shale.* This occurs in large quantities in nature, and consists of coal, clay, and iron pyrites. When it is heated in contact with the air the coal burns, as do also the sulphur and pyrites, and sulphuric acid is formed. When allowed to lie for a time in contact with the air the iron pyrites is converted into sulphate and sulphuric acid. The latter acts upon the clay or aluminium silicate, forming aluminium sulphate, from which alum can easily be made. It is easier to treat the shale and similar substances with sulphuric acid directly, and this method is now generally employed.

Alum dissolves readily in hot water, 357.5 parts of the crystallized salt dissolving in 100 parts of water at 100°. At 0° only 3.9 parts dissolve, and at the ordinary temperature about 12 parts. It crystallizes beautifully in regular octahedrons, occasionally with cube faces developed on them. Under some circumstances it crystallizes in cubes. When heated, alum melts in its water of crystallization, and if heated to a sufficiently high temperature the water passes off, leaving *burnt alum.* Heated higher the salt decomposes, forming aluminium oxide and potassium sulphate, and finally potassium aluminate is formed. When potassium hydroxide, ammonia, or the carbonate of potassium, sodium, or ammonium, is added in small quantity to a solution of alum the precipitate first formed redissolves. If this is continued until the reaction is neutral, or until a point is reached beyond which the addition of the reagent produces a precipitate which does not redissolve, there is then contained in the solution a basic compound, known as *basic alum,* which probably has the composition $K_2(Al_2O)(SO_4)_3$.

When the solution is boiled the salt contained in it is decomposed, forming ordinary alum and another basic alum which is insoluble :

$$3[K_2(Al_2O)(SO_4)_3] = K(AlO)_3(SO_4)_2 + 3KAl(SO_4)_2 + K_2SO_4.$$

The insoluble compound is known as *insoluble alum*.

Alum crystallized in cubes is obtained by evaporating a solution to which some sodium or potassium carbonate has been added. Alum is used very extensively in the preparation of pigments, as a mordant, in the sizing of paper, for clarifying water, etc.

**Ammonium Alum, Ammonium - Aluminium Sulphate, $(NH_4)Al(SO_4)_2 + 12H_2O$,** is in every way much like the potassium compound, and can be used in place of it for almost all purposes for which alum is used. It is somewhat more easily soluble than ordinary alum. As it is cheaper than the latter it is largely manufactured in place of it.

**Sodium Alum** is much more easily soluble in water than either potassium or ammonium alum, and this makes it difficult to prepare it in pure condition. It is therefore not manufactured, although sodium compounds are cheaper than those of either potassium or ammonium.

**Aluminium Silicate.**—It has been stated that aluminium silicate enters into the composition of a number of important minerals. It occurs in enormous quantities in nature. The most important of the minerals containing it are the feldspars, of which ordinary feldspar, $KAlSi_3O_8$, and albite, or sodium feldspar, $NaAlSi_3O_8$, are the most abundant. These again enter into the composition of granite together with quartz and mica, and mica is itself a double silicate of aluminium. As remarked under Silicic Acid (which see), the natural silicates are for the most part salts of polysilicic acids which are derived from orthosilicic acid by loss of water from two or more molecules. Up to the present but little more has been done with the many natural silicates than to determine their percentage composition. It appears probable from

what has already been learned regarding their constitution that investigations in this direction will before long yield interesting results. As yet, however, the methods for such investigations are quite unsatisfactory, owing largely to the fact that the compounds are so extremely stable that but few reagents decompose them, and if they are decomposed at all, the products are such that no conclusion can be drawn regarding the constitution. A careful study of the relations in which minerals occur in nature will undoubtedly be of assistance, as this will throw some light upon the conditions under which they were formed.

One of the most common decompositions of minerals, constantly taking place, and that has taken place to an enormous extent, is that of feldspar. Under the influence of moisture and the carbon dioxide of the air, this substance slowly decomposes, the products being mainly potassium or sodium silicate and aluminium silicate. The salt of the alkali metal, principally potassium, being soluble, is carried away, and finds its way into the soil. The silicate of aluminium is not soluble, but it easily forms emulsions with water, and is therefore carried down the sides of the hills and mountains upon which it is formed into the valleys, and much of it finds its way into streams. Sometimes this carrying away is prevented, and then large beds of comparatively pure clay, known as kaoline, are formed. The clay found in the valleys is always more or less impure and colored.

*Kaoline.*—This is the purest form of aluminium silicate found in nature. It always contains water. Its composition varies, some specimens on analysis giving results which lead to the formula $Al_4(SiO_4)_3 + 4H_2O$, according to which the substance is the salt of normal silicic acid, $Si(OH)_4$. Other specimens have the compo-

sition $HAlSiO_4 + H_2O$, or $Si \begin{cases} OH \\ O \\ O{\Rightarrow}Al + H_2O \\ O \end{cases}$. When

heated alone kaoline does not melt; but if feldspar is added to it, the whole melts, and forms a translucent mass known as *porcelain*. Other substances besides feldspar may be used for this purpose.

*Clay.*—Ordinary clay, as has been stated, is a name given to the impure varieties of aluminium silicate which have been carried down from the place of formation. Among the substances besides aluminium silicate found in clays are calcium carbonate, magnesium carbonate, sand, and hydroxides of iron. The color is largely determined by the amount of the hydroxides of iron present. The better varieties are used in the manufacture of the so-called "stone-ware," gas-retorts, and fire-bricks. The colored varieties are used for making ordinary earthenware and bricks. *Marl* is clay mixed with considerable quantities of calcium carbonate.

*Ultramarine.*—The substance occurring in nature and known as *lapis lazuli* consists of a silicate of sodium and aluminium together with a sulphur compound, probably a polysulphide of sodium. The coloring matter, known as ultramarine, obtained by powdering it was formerly very expensive, but it is now made artificially by the ton, and the color of the artificially prepared substance is even more beautiful than that of the natural. A great deal of work has been done in the way of investigating the chemical constitution of ultramarine, but the problem has not yet been fully solved. The artificial preparation is effected by melting together kaoline, anhydrous sodium carbonate, and sulphur; or clay, calcined sodium sulphate, and charcoal. By varying the conditions of the preparation products of different colors are obtained. Besides the deep-blue ultramarine, there are now manufactured ultramarines of different shades of blue, and a green variety. A white, a red, a yellow, and a violet variety are also known. The substance which gives to ultramarine its color is destroyed by acids, but not by alkalies. It can be heated in a closed vessel without change, but if heated to a high temperature in the air or in oxygen the color is destroyed.

Ultramarine is now manufactured in very large quantity—according to a recent report, to the extent of nearly 9000 tons a year. It is the most extensively used blue coloring matter.

*Porcelain.*—It was stated above that when kaoline is heated alone it does not melt, but that if feldspar is added to it, or if that found in nature contains feldspar, as is frequently the case, it either fuses together forming a compact mass, or it melts and forms a translucent mass. Further, when kaoline or any other variety of clay is mixed with water, a plastic substance results, which can be kneaded and worked into any desired form. These facts form the basis of the manufacture of earthenware, porcelain, etc. The ease with which the mass melts depends upon the quantity of feldspar or other flux added to it. If but little is added it melts with difficulty ; if much is added it melts easily.

In the manufacture of the finest kinds of porcelain kaoline is used. This is generally mixed with a little feldspar or chalk, gypsum or some other flux, and sand is also added. All these substances must be very finely ground. The mixture is then worked into the desired forms, and carefully dried. After the objects are dried they are next burned, first at a red heat at which the mass becomes solid, afterwards at a white heat for the purpose of forming a glaze upon the surface. The product after the first burning is that which is familiar as porous earthenware ; that formed in the second burning is the porcelain with glaze as it is commonly used.

In order to form the glaze upon the porcelain the porous earthenware first formed is drawn through a vessel containing proper materials in finely powdered condition and suspended in water. The materials used are generally the same as those used for the porcelain itself, but they are mixed in different proportions, with less kaolin, and more sand and feldspar, so as to be more easily fusible. After this treatment the objects are again heated to a high temperature.

*Earthenware.*—The ordinary varieties of earthenware are made from varieties of clay which are much less pure

than kaoline. Ordinary colored clay is used. The objects are formed, and then subjected in general to the same kind of treatment as porcelain. They are glazed in different ways. One method consists in bringing the glazing material on the earthenware before it is burned ; another method consists in putting the objects in the furnace without a glaze, and towards the end of the firing process sodium chloride is thrown into the furnace, and is thus brought in contact with the ware in the form of vapor. A chemical change takes place, resulting in the formation of a silicate of aluminium and sodium upon the surface. This melts, and forms a glaze.

Bricks are the most common variety of unglazed earthenware. Owing to the presence of other substances besides aluminium silicate, as, for example, calcium carbonate, the material is comparatively easily fusible. The color of bricks is largely due to the presence of oxides of iron.

**Reactions of Aluminium Salts which are of Special Value in Chemical Analysis.**—*Potassium* and *sodium hydroxides* precipitate aluminium hydroxide, which is soluble in an excess of the reagents.

*Ammonia* precipitates the hydroxide, which is only slightly soluble in an excess of the reagent.

*Hydrogen sulphide* and *carbon dioxide* precipitate aluminium hydroxide from a solution of an aluminate ; that is, from a solution of aluminium hydroxide in a caustic alkali.

*Ammonium sulphide* and other soluble sulphides precipitate the hydroxide. This is due to the instability of the sulphide of aluminium, or, going farther back, to the weak basic character of the hydroxide. The reaction of ammonium sulphide with aluminium sulphate takes place as represented in the following equation :

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 3(NH_4)_2SO_4 + 3H_2S + 2Al(OH)_3.$$

*Soluble carbonates* precipitate aluminium hydroxide for the same reason that the soluble sulphides do. The re-

action between aluminium sulphate and sodium carbonate takes place thus :

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 3Na_2SO_4 + 3CO_2 + 2Al(OH)_3.$$

### OTHER MEMBERS OF FAMILY III, GROUP A.

**Scandium, Sc (At. Wt. 43.78).**—This element was discovered in 1880 in the minerals euxenite and gadolinite. Its compounds are similar to those of aluminium. It forms an oxide of the formula $Sc_2O_3$; a sulphate, $Sc_2(SO_4)_3$; a double sulphate, $KSc(SO_4)_2$; etc. It is of special interest for the reason that its properties were foretold by Mendeléeff several years before it was discovered. The prophecy was based upon the position of the element in the periodic system. When the relations between the atomic weights and properties of the elements were first described in a comprehensive way by Lothar Meyer and Mendeléeff, the latter described the properties of an element then unknown, which he called *ekaboron*. This should have the atomic weight about 44, should form an oxide of the formula $M_2O_3$, etc. It has been shown that the properties of scandium agree very closely with those foretold.

**Yttrium, Y (At. Wt. 88.35),** like scandium, is found in gadolinite, euxenite, and some other rare minerals. The element itself has not been isolated. Its *chloride*, $YCl_3 + 6H_2O$, is easily made. With potassium and sodium chlorides it forms double chlorides analogous to those formed by aluminium chloride. Its *oxide* has the formula, $Y_2O_3$, and is formed by heating the hydroxide, $Y(OH)_3$, or nitrate, $Y(NO_3)_3$. The *hydroxide*, $Y(OH)_3$, is precipitated by adding potassium hydroxide to a solution of an yttrium salt, and is not dissolved by an excess of the alkali. The hydroxide, while being less acidic than aluminium hydroxide, is also more strongly basic, as is shown by its power to unite with weak acids. When exposed to the air, it attracts and combines with carbonic acid.

**Ytterbium, Yb (At. Wt. 171.88).**—This rare element, like scandium and yttrium, is found in gadolinite and euxenite—most abundantly in the latter. Its compounds in general resemble those of yttrium. Its hydroxide is not soluble in alkalies, but it absorbs and combines with carbon dioxide. Its oxide has the formula $Yb_2O_3$, its sulphate, $Yb_2(SO_4)_3$, etc.

**Samarium, Sm, Terbium, Tr, and Gadolinium, Gd,** are elements that have been obtained from samarskite, a North Carolina mineral. They have also been found in small quantities in some other minerals, as cerite, gadolinite, and orthite. In general these elements resemble aluminium in their chemical conduct.

**Helium.**—When cleveite and some other rare minerals are treated with acids a gas is given off. This was at first held to be nitrogen, but a careful spectroscopic examination by W. Ramsay has shown that it contains a hitherto unknown gas. The spectrum contains lines which are identical with lines that have been observed in the solar spectrum. These have been ascribed to an unknown element, *helium.* This has now been isolated and studied. It proves to be a very light gas, as incapable of forming chemical compounds as argon. Practically all the evidence goes to show that it is an element, but as yet little is known in regard to its relations to other elements.

The chemistry of *lanthanum* is so intimately connected with that of cerium and didymium, that, although these three elements appear to belong to different families, they will be briefly considered together.

**The Boron-Aluminium Group in General.**—Comparing the group of which boron and aluminium are the principal members with the potassium, calcium, and magnesium groups, it will be seen that the members of this group do not resemble one another as closely as the members of the other groups do. There is, however, the same strengthening of the basic properties and weakening of the acid properties as the atomic weight increases. Boron is the most strongly acid and the least basic; aluminium is more basic, but has still some acid prop-

erties ; while the other members are more strongly
basic, and do not exhibit any acid properties. Compar-
ing the first members of Group A, of Families I, II, and
III, it is clear that with increasing atomic weight the
acid properties and the valence increase. The elements
referred to are lithium, glucinum, and boron.

**Members of Group B, Families I, II, III, and IV.**—The
base-forming elements thus far considered form the prin-
cipal groups of the first three families. In these principal
groups the most characteristic elements of these families
occur. But besides the principal group of each family
there is a secondary group, the members of which differ
in some respects from those of the principal group,
though they resemble one another. Between the second-
ary group of Family I and that of Family II, further,
there are some points of resemblance. The secondary
group in Family IV bears to the principal group much
the same relation that the secondary groups of the first
three families bear to the principal groups. In the table
p. 151 the principal groups are those which fall under
the letter A, and the secondary groups are those which
fall under the letter B in each of the first four families.
These secondary groups are :

| Family | Group | | | |
| --- | --- | --- | --- | --- |
| I | B | Copper | Silver | Gold |
| II | B | Zinc | Cadmium | Mercury |
| III | B | Gallium | Indium | Thallium |
| IV | B | Germanium | Tin | Lead |

In the fifth, sixth, and seventh families the most char-
acteristic elements are those which occur in Group B.
These have already been studied.

Having thus considered the members of the principal
groups of the first four families, let us next turn to the
study of the members of the secondary groups.

# CHAPTER XXVIII.

**General.**—The facts which strike one most forcibly on comparing the elements of this group with those of Group A of the same family are, that they are much less active chemically, and that they furnish a greater variety of compounds. Sodium and potassium and the other members of Group A display the greatest activity, as we have seen. The basic character is most strongly developed in them. Further, in nearly all their compounds they act with the same valence. They are univalent in all their salts. Copper, silver, and gold, however, are not chemically active elements, and the activity grows less with increasing atomic weight. Copper and gold form two series of compounds each, and silver also forms a few compounds, in which it appears with a valence greater than one. In the two series of salts formed by copper the element appears to be univalent and bivalent, as in the chlorides $CuCl$ and $CuCl_2$. Gold, however, is univalent and trivalent, while silver is almost exclusively univalent. It must be said that the resemblance between gold and the other members of Group B is apparently not as marked as that between mercury and copper and silver. It is, however, possible that as investigation proceeds the resemblance will appear more striking than it does at present.

## COPPER, Cu (At. Wt. 63.12).

**General.**—The compounds of copper which are most commonly met with are those in which it acts as a bivalent element. Its principal compounds are *copper oxide,*

CuO ; the *sulphate*, $CuSO_4$; and the *sulphide*, CuS. In all these the copper is bivalent. But besides these there are such compounds as CuCl and $Cu_2O$, in which the element appears to be univalent. There are, then, two series of salts, of which the following will serve as examples :

<div align="center">

| | |
|---|---|
| CuCl | $CuCl_2$ |
| CuBr | $CuBr_2$ |
| $Cu_2O$ | CuO |

</div>

Those compounds which are of the first order, corresponding to the chloride CuCl, are called *cuprous compounds*. Thus, CuCl is *cuprous chloride;* $Cu_2O$, *cuprous oxide*, etc. On the other hand, compounds of the second order are called *cupric compounds*. Thus, $CuCl_2$ is *cupric chloride;* CuO, *cupric oxide;* $CuSO_4$, *cupric sulphate*, etc. It has been suggested that perhaps the formula of the simpler cuprous compounds, like CuCl, etc., should be doubled, and written $Cu_2Cl_2$, $Cu_2I_2$, etc. This suggestion has its origin in the valence hypothesis. In cupric chloride, $CuCl_2$, and cupric oxide, CuO, copper is evidently bivalent; whereas, if the formulas of the cuprous compounds are the simpler ones, CuCl, CuI, etc., copper is univalent in them. If, however, cuprous chloride is $Cu_2Cl_2$, it may be that in it the copper is bivalent. It is only necessary to assume that in the molecule of cuprous chloride two atoms of copper are combined as represented thus :

<div align="center">

Cu–
|
Cu–

</div>

If, then, each of the copper atoms should combine with a chlorine atom, the compound would have the formula $Cu_2Cl_2$. The question here presented is similar to that concerning the molecular formula of aluminium chloride. A determination of the specific gravity of the vapor of cuprous chloride has been made, and it has been found to correspond to that required by the formula $Cu_2Cl_2$. It is possible, however, that at a higher temperature a different result may be obtained, as in the case of alu-

minium chloride, and it is possible that the compound may be a double chloride, formed by union through the chlorine atoms as represented in the formula CuCl–ClCu or Cu–(Cl$_2$)–Cu.   Then there would be complete analogy between cuprous chloride and cuprous oxide, Cu–O–Cu. Our knowledge in regard to this matter is extremely limited at present, and it seems perfectly justifiable to use the simpler formulas for the cuprous compounds until further evidence has been produced.   Whatever the explanation may be, it is undoubtedly a fact that there are two series of salts of copper, in one of which there is relatively half as much copper as in the other, and it is also a fact that by comparatively simple methods the salts of one series can be converted into those of the other, as will be pointed out below.

**Forms in which Copper occurs in Nature.**—Copper is a widely distributed element, and it occurs also in large quantities.   It occurs in the uncombined condition, or as *native copper*, in large quantity in the United States in the neighborhood of Lake Superior, in China, Japan, Siberia, and Sweden.   The most valuable ores of copper are the oxides, *ruby copper* or cuprous oxide, Cu$_2$O, and cupric oxide, CuO; the carbonates, as malachite, Cu$_2$(OH)$_2$CO$_3$; the sulphides, as chalcocite, Cu$_2$S, copper pyrites, Cu$_2$S.Fe$_2$S$_3$; and others.

**Metallurgy of Copper.**—The metallurgy of copper is comparatively complicated, owing to the difficulty of converting the ores of copper into the oxide.   In most of the ores used sulphur and iron are contained, as well as smaller quantities of other elements, as arsenic, antimony, lead, etc.   The ores are first roasted with the object of converting the sulphides partly into oxides. Under these circumstances the sulphides of iron are more easily converted into the oxides than the sulphides of copper.   By adding a material rich in silicic acid, and melting the roasted ore in a blast furnace with charcoal, the oxide of iron is partly reduced, and converted into silicate, which runs off with the slag.   In this way a product is obtained which is richer in copper than the roasted ore.   This, which is called the *matte*, contains

copper sulphide and iron sulphide. The *matte* is again roasted and melted in the same way as the ore, and a further quantity of iron is removed, while some of the copper is reduced. A reaction which plays an important part in these processes is that which takes place between cuprous oxide and cuprous sulphide, forming metallic copper and sulphur dioxide:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Sometimes it is necessary to repeat the roasting and melting with charcoal and sand a number of times, the matte becoming richer in copper at each successive stage.

**Properties.**—Copper is a hard metal, of a reddish color and metallic lustre. It does not change in dry air, but in moist air it gradually becomes covered with a green layer of a basic carbonate. It melts at a somewhat lower temperature than gold, and at a somewhat higher temperature than silver. It is very malleable and tenacious. It decomposes water only at bright-red heat. When heated in the air to a comparatively high temperature it becomes covered with a layer of cupric oxide; at a lower temperature cuprous oxide is formed. Nitric acid dissolves it, copper nitrate, $Cu(NO_3)_2$, being formed, and the oxides of nitrogen being evolved (see p. 285); dilute sulphuric acid does not act upon it unless the air has access to it; concentrated sulphuric acid when heated with it forms cupric sulphate, $CuSO_4$, and sulphur dioxide (see p. 217). Dilute acids in general do not act upon it unless the air has access to it. This fact is of importance in connection with the use of copper vessels in culinary operations. Substances containing vegetable acids can be boiled in bright copper vessels with impunity, for the water vapor prevents the access of air, but, on cooling, the air is admitted, and then action takes place, causing solution of some of the copper, which is objectionable. Ammonia in contact with copper absorbs oxygen, and the copper dissolves in consequence of the formation of a compound of cupric oxide and ammonia. This fact is sometimes taken advantage of for

the preparation of nitrogen, as was stated in speaking of this gas (see p. 249).

**Applications.**—As is well known, copper is used very extensively for a variety of purposes, among which the following may be mentioned : for electrical apparatus, coins, copper vessels, roofs, for covering the bottoms of ships, etc. It is also used for copper-plating ; and in the preparation of a number of valuable alloys, such as brass, bronze, gun-metal, bell-metal, etc.

**Alloys.**—*Brass* is a mixture or compound of about one part of zinc and two parts of copper ; these proportions may, however, be varied between quite wide limits. There is a variety of brass containing equal parts of zinc and copper, and another containing one part of zinc and five parts of copper. *Pinchbeck* is made by combining two parts of copper and one of brass.

*Bronze* consists of copper, zinc, and tin. The proportion of copper varies from 65 to 84 per cent ; that of zinc from 31.5 to 11 per cent ; and that of tin from 2.5 to 4 per cent. When exposed to the air bronze becomes covered with a green coating of basic copper carbonate, which protects it from further action. This coating is now generally produced artificially by a variety of methods, as by washing the surface with a solution of salts and acids.

*Gun-metal* consists generally of copper and tin in the proportion of 11 parts of tin and 100 parts of copper.

*Bell-metal* contains a larger proportion (from 20 to 25 per cent) of tin than gun-metal.

*Alloys with Aluminium* containing aluminium and copper in widely different proportions are made. That with 3 per cent of copper has a whiter color than aluminium, the color being more like that of silver. On the other hand, an alloy of copper with 5 to 10 per cent of aluminium has a color resembling that of gold. This, which is known as aluminium bronze, is very hard and elastic, and is not easily acted upon by chemical reagents. It is now used to a considerable extent in the manufacture of ornamental and useful articles.

*German silver* is an alloy consisting of copper, zinc, and

nickel. The proportion of copper varies from 40 to 60 per cent; that of zinc from 19 to 44 per cent; and that of nickel from 6 to 22 per cent.

**Cuprous Hydride, CuH.**—This compound is made by treating a solution of barium hypophosphite with a solution of copper sulphate. It is thrown down as a yellow precipitate which gradually becomes darker. At 60° it decomposes into copper and hydrogen. With hydrochloric acid it yields cuprous chloride and hydrogen.

**Cupric Hydride, $CuH_2$,** is formed by treating a solution of copper sulphate with hypophosphorous acid. When freshly prepared it is a reddish-brown sponge-like mass, which, however, changes to a chocolate-colored powder on being freed from acid and boiled for some time. It is not readily changed when heated in the air. It dissolves in hydrochloric acid with evolution of hydrogen.

**Cuprous Chloride, CuCl,** is formed by heating cupric chloride, $CuCl_2$; by passing hydrochloric acid over highly heated copper; by boiling an excess of copper filings with concentrated hydrochloric acid with the addition of a little nitric acid, filtering through asbestos, and pouring into water; and by treating cupric chloride with reducing agents, as, for example, sulphurous acid. The action with sulphur dioxide takes place as represented in the equation

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + H_2SO_4 + 2HCl.$$

It is a white crystalline compound, and is difficultly soluble in water. When exposed to the air it rapidly turns green in consequence of the formation of a basic chloride, as, for example, $2CuO.CuCl_2$, or Cl–Cu–O–Cu–O–Cu–Cl. It is volatile at a high temperature, and a determination of the specific gravity of the vapor gave a result corresponding to the formula $Cu_2Cl_2$, as was stated above. It has markedly the power to absorb chlorine, and therefore acts as a reducing agent. Ammonia dissolves it, forming a compound of the composition represented by the formula $CuCl.NH_3$, which may be regarded as derived from ammonium chloride by replacing an atom of hydrogen by an atom of copper.

**Cupric Chloride, $CuCl_2$.**—This compound is formed by treating copper or cuprous chloride with chlorine. It is

also easily made by dissolving cupric hydroxide, or carbonate, in hydrochloric acid. From its solution in water the chloride crystallizes with two molecules of water, $CuCl_2 + 2H_2O$. The crystals when heated lose their water without suffering further decomposition, except at high heat, when a part of the chlorine is given off, and cuprous chloride is formed. Cupric chloride combines with ammonia gas, forming a compound of the formula $CuCl_2.6NH_3$, which is soluble in water, with a dark blue color. When heated it loses four molecules of ammonia, and the compound $CuCl_2.2NH_3$ is left behind. This may be regarded as ammonium chloride, in which two hydrogen atoms have been replaced by an atom of bivalent copper, as represented in the formula $Cu < ^{NH_3Cl}_{NH_3Cl}$. There is, however, no direct experimental evidence in favor of this view.

With other chlorides cupric chloride forms double chlorides similar to those formed by magnesium and aluminium; such, for example, as $CuCl_2.2NH_4Cl$ or $(NH_4)_2CuCl_4$, $CuCl_2.2KCl$, or $K_2CuCl_4$, etc.

**Cuprous Iodide, CuI.**—When a solution of a cupric salt is treated with potassium iodide, cuprous iodide is precipitated and iodine is set free, owing to the instability of cupric iodide:

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2.$$

If a reducing agent is added at the same time, iodine is not set free. Thus, for example, when sulphur dioxide is used, the reaction takes place as represented in the equation

$$2CuSO_4 + SO_2 + 2KI + 2H_2O = K_2SO_4 + 2H_2SO_4 + 2CuI.$$

It forms a white precipitate. Cupric iodide is not known. A similar conduct is shown by the cyanides.

**Cuprous Hydroxide, Cu(OH).**—The simple compound of the formula here given is not known, but a derivative of this, of the formula $Cu_8O_3(OH)_2$ or $4Cu_2O.H_2O$, is easily made by adding sodium hydroxide to a solution of

a cuprous salt. It passes readily over into cuprous oxide by gently heating it.

**Cuprous Oxide, $Cu_2O$,** occurs in nature, and is known as *ruby copper* or *cuprite*. It is easily prepared by treating a solution of glucose, or starch sugar, with copper sulphate and potassium hydroxide. By boiling, the copper is thrown down in the form of cuprous oxide. At first this is yellow, and it is supposed by some that the yellow compound is the hydroxide, but satisfactory evidence of the correctness of this view has not been furnished. The yellow precipitate is soon converted into the red oxide. Cuprous oxide is not changed when allowed to lie in contact with the air. It dissolves in nitric and sulphuric acids, forming cupric salts; and if the acids are dilute, copper is deposited. This will be clear from a consideration of the following equation:

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu.$$

**Cupric Hydroxide, $Cu(OH)_2$,** like the hydroxides of most base-forming elements, is thrown down by the addition of a soluble hydroxide to a cupric salt. It is a voluminous, blue precipitate. When allowed to stand in a solution, or when the solution is boiled, the hydroxide loses a part of its hydroxyl, and is converted into a black compound of the formula

$$Cu(OH)_2 + 2CuO, \text{ or } HO–Cu–O–Cu–O–Cu–OH,$$

and this when dried and heated is converted into the oxide $CuO$.

**Cupric Oxide, $CuO$.**––Cupric oxide is found in nature in the neighborhood of Lake Superior in the United States, and is formed by heating copper to redness in contact with the air, or by heating the nitrate. It loses its oxygen very readily when treated with reducing agents, such as hydrogen and carbon. It is used extensively in quantitative analysis for the purpose of estimating the composition of organic compounds, or such as contain carbon and hydrogen. Its use is based upon the fact that when organic compounds are heated with the oxide

they are oxidized, the carbon being converted into carbon dioxide and the hydrogen into water. By passing the products of the oxidation through calcium chloride, and a solution of potassium hydroxide, the water is retained in the first, and the carbon dioxide in the second, and the weight of each formed can easily be determined. Cupric oxide is dissolved by ammonia in the presence of air and a little of some ammonium salt. The composition of the compound in the solution is not known.

**Other Oxides of Copper.**—Besides cuprous and cupric oxides, copper forms two other compounds with oxygen. These are *copper suboxide*, $Cu_4O$, and the *peroxide*, $CuO_2$. The former is prepared by treating a solution of copper sulphate with stannous chloride. It takes up oxygen from the air, and is converted into higher oxides. The peroxide is said to be formed by treating cupric hydroxide with hydrogen peroxide.

**Cupric Sulphate, $CuSO_4$.**—This salt is manufactured on the large scale, and in the crystallized form, containing five molecules of water, $CuSO_4 + 5H_2O$, is commonly called "blue vitriol." It is found in nature to some extent, being formed by the action of the oxygen of the air on the sulphide. It is most conveniently made by dissolving metallic copper in concentrated sulphuric acid, or by treating cupric sulphide with sulphuric acid. The action of sulphuric acid on the metal has already been referred to. It consists essentially in the formation of cupric sulphate, sulphur dioxide, and water, as expressed in the equation

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The question whether the copper reduces the sulphuric acid directly, or the hydrogen given off from the acid effects the reduction, is an open one. But there are other products formed besides those mentioned. At first a brown substance of the composition $Cu_2S$ is deposited. As the action proceeds oxysulphides are formed, the final product of a series of changes being $Cu_2OS$, or $CuO.CuS$, which is black, and insoluble in water. Under some conditions a considerable proportion

of the copper is transformed into the oxysulphides by sulphuric acid. Cupric sulphate is obtained in large blue crystals of the triclinic system, which have the composition $CuSO_4 + 5H_2O$. When heated to 100°, four molecules of water are given off, and the last is not given off until the temperature 200° is reached. This makes it appear probable that the salt has the constitution represented by the formula $CuSO_2(OH)_2$ or

$$OS \begin{cases} O \\ O \end{cases} > Cu \\ OH \\ OH$$ , corresponding in this respect to magnesi-

um sulphate (which see). When heated higher, it loses all its hydroxyl, and the salt, $CuSO_4$, is left in the form of a white powder, which has the power to take up water from the air, becoming blue again. It dissolves in three parts of cold water and one-half part boiling water. Copper sulphate, containing seven molecules of water, $CuSO_4 + 7H_2O$, is obtained when mixed with solutions of the sulphates of iron, zinc, or magnesium, all of which crystallize with seven molecules of water. In this form cupric sulphate is isomorphous with the other sulphates. These salts have in general received the name of vitriols, and the old names " green vitriol," " white vitriol," and " blue vitriol" are still used to some extent, though rarely by chemists. Among the similar salts included under the same general head are the following:

| | |
|---|---|
| Zinc sulphate (white vitriol), . . . . . | $ZnSO_4 + 7H_2O$ |
| Magnesium sulphate,. . . . . . . . | $MgSO_4 + 7H_2O$ |
| Glucinum sulphate, . . . . . . . . | $GlSO_4 + 7H_2O$ |
| Ferrous sulphate (green vitriol), . . . | $FeSO_4 + 7H_2O$ |
| Nickel sulphate, . . . . . . . . . | $NiSO_4 + 7H_2O$ |
| Cobalt sulphate, . . . . . . . . . | $CoSO_4 + 7H_2O$ |
| Copper sulphate (blue vitriol), | |

$$CuSO_4 + 7H_2O, (CuSO_4 + 5H_2O)$$

Cupric sulphate is used extensively in the preparation of blue and green pigments, in copper-plating by electrolysis, in galvanic batteries, for the purpose of preserving wood, and as a remedy against *phylloxera* (see p. 406), etc.

Cupric sulphate combines with other sulphates, forming double salts similar to those formed by aluminium and magnesium. The potassium and ammonium compounds have the formulas $K_2SO_4.CuSO_4 + 6H_2O$ and $(NH_4)_2SO_4.CuSO_4 + 6H_2O$, and probably have the constitution represented by the general formula

$$SO_2 \overset{\displaystyle OM}{\underset{\displaystyle O}{<}} \overset{}{\underset{\displaystyle O}{}} \overset{}{>} Cu.$$
$$SO_2 \overset{\displaystyle O}{\underset{\displaystyle OM}{<}}$$

When a solution of cupric sulphate is treated with ammonia a precipitate of a basic salt is at first formed, but this dissolves when more ammonia is added, forming a deep-blue solution. The precipitate first formed is a basic sulphate of copper; while the solution contains a compound of cupric sulphate, ammonia, and water, of the composition represented by the formula $CuSO_4.4NH_3 + H_2O$. When heated the salt loses water and ammonia, until it has the composition $CuSO_4.2NH_3$. This is probably analogous to the ammonia compound of cupric chloride, $CuCl_2.2NH_3$, and may be regarded as having a similar constitution, that is, as ammonium sulphate, in which two hydrogen atoms have been replaced by an atom of bivalent copper, as expressed in the formula $SO_4 \overset{\displaystyle NH_3}{\underset{\displaystyle NH_3}{<}} > Cu$. It is a curious and interesting, though at present inexplicable, fact, that anhydrous copper sulphate combines with five molecules of ammonia just as it does with five molecules of water, and that by lying in moist air the molecules of ammonia in the compound are successively replaced by water, so that the following series of compounds is formed:

$$CuSO_4.5NH_3\,;$$
$$CuSO_4.4NH_3.H_2O\,;$$
$$CuSO_4.3NH_3.2H_2O\,;$$
$$CuSO_4.2NH_3.3H_2O\,;$$
$$CuSO_4.NH_3.4H_2O\,;$$
$$CuSO_4.5H_2O.$$

From this it would appear that the ammonia in these compounds plays a part analogous to that played by the " water of crystallization." This does not speak in favor of the view above expressed concerning the constitution of cuprammonium sulphate, in which the copper is held to be in combination with nitrogen. There is in fact no satisfactory theory for most of the salts containing water of crystallization, nor for most of those containing ammonia. The power to combine with ammonia is very commonly met with among metallic salts—probably fully as much so as the power to combine with water. Some metals indeed, as cobalt and platinum, form a very large number of complex compounds with ammonia, and with ammonium salts.

**Cupric Nitrate, $Cu(NO_3)_2$,** is easily formed by dissolving copper in dilute nitric acid. It is easily soluble in water, and is deposited in crystallized form, the crystals containing three or six molecules of water according to the temperature, the salt with six molecules being formed at the lower temperature. Like other copper salts, it has a blue color. It combines with ammonia and with ammonium nitrate.

**Cupric Arsenite, $CuHAsO_3$,** is formed as a greenish-yellow precipitate when an ammoniacal solution of arsenious acid is added to a solution of cupric sulphate. It is known as *Scheele's green.* A compound of cupric arsenite and cupric acetate, which is made by treating a basic acetate of copper with arsenious acid, is known as *Schweinfurt green.* On account of their poisonous character these compounds are not now used as extensively as formerly.

**Cupric Carbonates.**—When a soluble carbonate is added to a solution of cupric sulphate a voluminous greenish precipitate is formed, which has the composition

$$Cu(OH)_2.CuCO_3, \quad \text{or} \quad \begin{matrix} Cu{<}{OH \atop O} \\ Cu{<}{O \atop OH} \end{matrix}{>}CO. \quad$$

This is plainly a basic carbonate. The mineral malachite, which has a beautiful green color, has the same composition as the precipitate just mentioned.

**Cyanides of Copper.**—Both cuprous and cupric cyanides are known, but while generally the cupric compounds are the more stable, cupric cyanide, like cupric iodide, is extremely unstable. It is readily changed to a compound intermediate between the cupric and the cuprous salt. This has the composition $CuCy_2.2CuCy$. By heating in suspension in water this intermediate compound is converted into the cuprous salt. The cuprous compound is quite stable. Cupric cyanide is formed as a yellow precipitate, when potassium cyanide is added to a solution of a copper salt. It soon changes spontaneously into the compound above mentioned, which has a green color. When this is heated it yields cuprous cyanide, $CuCN$, which is white. Cuprous cyanide is insoluble in water. If an excess of potassium cyanide is added to a solution of a copper salt, the precipitate dissolves in consequence of the formation of double cyanides similar to the double chlorides. One of these has the composition $KCN.CuCN$ or $KCu(CN)_2$. The one formed under ordinary circumstances is $3KCN.CuCN$ or $K_3Cu(CN)_4$. The double cyanides are in general more complicated in composition than the double chlorides, as we shall see in studying those which contain iron—such, for example, as the salt already referred to under the name potassium ferrocyanide or yellow prussiate of potash, of the composition $K_4Fe(CN)_6$.

**Cuprous Sulphocyanate, CuSCN,** and **Cupric Sulphocyanate, Cu(SCN)₂,** bear to each other relations similar to those which exist between the cyanides. When potassium sulphocyanate is added to a concentrated solution of a cupric salt cupric sulphocyanate is precipitated as a black powder. If the solution is diluted, decomposition into the cuprous salt takes place. When a reducing agent such as sulphur dioxide is added at the same time, only the cuprous salt is formed. This is a white, granular powder, insoluble in water.

**Cuprous Sulphide, Cu₂S.**—This compound occurs in nature, and is known as chalcocite. It is, further, a constituent of copper pyrites, which is a compound of cuprous and ferric sulphides, $Cu_2S.Fe_2S_3$ or $CuFeS_2$. It

can be made by heating copper and sulphur together in the right proportions. It has a grayish-black color; does not give up its sulphur, even when heated in hydrogen; and is the more stable of the two sulphides of copper.

**Cupric Sulphide, CuS.**—This is formed as a black precipitate when hydrogen sulphide is passed into a solution of a cupric salt. In water alone cupric sulphide is somewhat soluble. Hence in washing out a precipitate of copper sulphide with water a little of it will pass through in solution. It also easily undergoes oxidation, and, as it forms the sulphate, some is dissolved in this way unless proper precautions are taken. It is slightly soluble in ammonium sulphide, but insoluble in sodium sulphide. The above facts are of importance in the analysis of compounds containing copper, as will readily be seen. When heated, cupric sulphide loses half its sulphur, and is converted into cuprous sulphide.

**Copper-plating.**—The process of copper-plating consists in brief in depositing upon an object a layer of copper by putting it in a bath containing some copper salt, and connecting it with one pole of an electric battery. Decomposition of the copper salt takes place, and copper is deposited upon the object. Alkaline solutions of the double cyanides are best adapted to the purpose. The process is extensively used in the preparation of *electrotype* plates. These are plates which are prepared either from wood-cuts or from type by making a mould of gutta-percha, covering this with graphite, and immersing the plate thus prepared in the copper-plating bath. The plate thus made is an exact reproduction of the wood-cut or type of which the impression in gutta-percha was taken.

**Reactions which are of Special Value in Chemical Analysis.**—*Potassium* or *sodium hydroxide* forms a blue precipitate which becomes black on standing or when heated. (See Cupric Hydroxide.)

*Ammonia* first forms a greenish precipitate, which is a basic salt. With cupric sulphate the reaction takes place thus:

$$SO_2<^O_O>Cu \atop SO_2<^O_O>Cu \quad + 2NH_3 + 2H_2O = \quad Cu<^{OH}_O>SO_2 + (NH_4)_2SO_4. \atop Cu<^O_{OH}}$$

If the action is carried farther, the basic salt dissolves, forming the compound referred to under Cupric Sulphate (which see), the solution being dark blue.

*Potassium or sodium carbonate* precipitates the basic carbonate referred to under Cupric Carbonate (which see). The change in color from blue to green which takes place in this precipitate is probably due to a loss of water.

*Potassium ferrocyanide*, $K_4Fe(CN)_6$, forms a reddish-brown precipitate, which is the corresponding copper salt, $Cu_2Fe(CN)_6$. This compound is decomposed by caustic alkalies, forming cupric oxide and the corresponding alkali salt, $Na_4Fe(CN)_6$ or $K_4Fe(CN)_6$. The reactions with potassium iodide, cyanide, and sulphocyanide have been explained above.

In the oxidizing flame the bead of borax or microcosmic salt is greenish blue, while when heated in the reducing flame it appears opaque and red. The red color is due to the reduction of the oxide to copper or cuprous oxide.

## SILVER, Ag (At. Wt. 107.11).

**General.**—In nearly all the compounds of silver the element is univalent. It, however, forms three oxides of the formulas $Ag_4O$, $Ag_2O$, and $AgO$. The compounds correspond closely in many respects to the cuprous compounds. There is the same question here as in the case of copper as to whether the molecular weights correspond to the simple formulas $AgCl$, $AgBr$, $AgNO_3$, etc., or to the doubled formulas $Ag_2Cl_2$, $Ag_2Br_2$, $Ag_2(NO_3)_2$, etc. There is no evidence at present known by which a decision between the two possibilities can be reached. The simpler formulas will therefore be used here.

**Forms in which Silver Occurs in Nature.**—Silver occurs to some extent native, but for the most part in combination, particularly with sulphur, and in company with

lead. The principal ore of silver is the sulphide, $Ag_2S$, which occurs in combination with other sulphides, as of lead, copper, arsenic, antimony, etc. The compounds with chlorine, bromine, and iodine are also found, but in smaller quantity than the sulphide. Small quantities of the sulphide are found in almost all varieties of galenite or lead sulphide.

**Metallurgy of Silver.**—Much of the silver in use is obtained from galenite, PbS. This mineral is treated in such a way as to cause the separation of the lead (which see), and the silver is separated from sulphur at the same time. But it is dissolved in a large quantity of lead, and the problem which presents itself to the metallurgist is how to separate the small quantity of silver from the large quantity of lead. This is accomplished by melting the mixture and allowing it to cool until crystals appear. These are almost pure lead. They are dipped out by means of a sieve-like ladle, and the liquid left is again allowed to stand, when another crop of crystals is formed, and can be removed in the same way as before. By this means, and by again melting the crystals removed, allowing the liquid to crystallize, and removing the crystals formed, there is finally obtained a product which is rich in silver, but which still contains lead. This is heated in appropriate vessels in contact with the air, when the lead is oxidized, while the silver remains in the metallic state. This method of concentrating by crystallization of lead is known as *Pattinson's method.*

Another method of separating lead and silver now extensively used consists in treating the molten alloy with a small quantity of zinc. This takes up all the silver, and the alloy of zinc and silver thus formed is removed, and afterwards treated with superheated steam, by which the zinc is oxidized and the silver left unchanged.

Some ores of silver are treated in another way, known as the *amalgamation process.* The ores are mixed with common salt and roasted, when the silver is obtained in the form of the chloride. This is then reduced to silver

by means of iron and water, the reaction taking place as represented in the following equation:

$$2AgCl + Fe = FeCl_2 + 2Ag.$$

The mixture is next treated with mercury, which forms an amalgam with silver, while the other metals present do not combine with the mercury. The amalgam can be separated from the rest of the mass without much difficulty, and when heated to a sufficiently high temperature the mercury distils over, leaving the silver.

A modification of the amalgamation process, known as the American process, consists in grinding the ores very fine, mixing them with sodium chloride, adding roasted copper pyrites, which consists largely of copper sulphate, and then gradually adding mercury. The silver is slowly converted into silver amalgam. The explanation of the process is this: The copper sulphate reacts with the sodium chloride to form cupric chloride and sodium sulphate. Cupric chloride reacts upon the silver sulphide as represented in the equation

$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S.$$

The cuprous chloride thus formed acts upon the rest of the silver sulphide, forming silver chloride and cuprous sulphide:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

The silver chloride dissolves in sodium chloride, and is then reduced and converted into the amalgam by the mercury.

The silver in the market is not pure. For chemical purposes it can be purified by dissolving it in nitric acid, precipitating by means of hydrochloric acid, filtering and thoroughly washing the chloride, and reducing this either by melting it with sodium carbonate, or by pouring a little dilute hydrochloric acid upon it, and bringing a piece of zinc in contact with it. In the former case the reaction is

$$2AgCl + Na_2CO_3 = 2Ag + CO_2 + O + 2NaCl;$$

in the latter it is

$$Zn + 2AgCl = ZnCl_2 + 2Ag.$$

**Properties.**—Silver is a white metal with a high lustre, of specific gravity 10.5. It is not acted upon by the air, oxygen, or water. It melts at a lower temperature than copper or gold, the melting-point being about 1000°. At the temperature of the oxyhydrogen blowpipe it distils, and in the experiments of Stas on the atomic weights of chlorine and silver the metal used was purified in this way. It is harder than gold and softer than copper, and its hardness is much increased by the addition of a little copper. It combines very readily with sulphur, forming black silver sulphide, and with chlorine, bromine, and iodine. The blackening of silver coins, and other objects carried about the person is caused by the presence of minute quantities of sulphur compounds in the perspiration; and the blackening of spoons by contact with eggs is due to the presence of sulphur in the albumen of the eggs. When pure silver is melted in the air it absorbs about twenty times its volume of oxygen, and this is given off when the metal solidifies, causing in some cases a sputtering of the silver. This phenomenon is observed in the separation of silver from its ores in those processes in which it is necessary to melt the metal. It is known as " spitting."

At the ordinary temperatures silver is converted into the peroxide, AgO, by ozone. When treated with hydrochloric acid, the metal becomes covered with a thin layer of the chloride, and no further action takes place, but it is dissolved easily by concentrated sulphuric acid and dilute nitric acid. With the concentrated acids reduction-products are formed as with copper. Silver is readily dissolved by a solution of potassium cyanide; hence, such a solution is used in removing stains caused by silver salts. It is not acted upon by the alkaline hydroxides nor by potassium nitrate in the molten condition, while platinum is. Therefore, silver vessels are used when it is desired to melt these substances in the

laboratory, or to evaporate their solution, as in the preparation of the caustic alkalies.

**Allotropic Forms of Silver.**—M. Carey Lea has discovered several curious allotropic forms of silver, the principal of which are briefly described by him as follows: "*A*. Soluble, deep red in solution, mat lilac, blue, or green while moist, brilliant bluish-green metallic when dry. *B*. Insoluble, derived from *A*, dark reddish-brown while moist, when dry somewhat resembling *A*. *C*. Gold silver, dark brown while wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-colored. Insoluble in water; appears to have no corresponding soluble form."

The form *A* is soluble in water, and the solution thus formed has a deep red color. The different varieties are formed by the action of reducing agents on solutions of silver salts. For example, the red soluble form is obtained by mixing dilute solutions of ferrous citrate and a silver salt. All the allotropic forms of silver are readily changed to the ordinary form.

Mr. Lea further says: "All the forms of allotropic silver are sensitive to light. *A* when exposed to the sunlight soon becomes brown. The bright blue-green variety of *B* is changed into the pure gold-colored variety of *C*. Other forms of *B* turn brown on exposure to light."

The red-yellow variety of *C* changes to bright gold color. "Continued exposure seems to produce little further change so long as the substance is dry. But if the paper on which the silver is placed is kept moist by a wet pad, with three or four days of good sunshine, the change goes on until the silver becomes perfectly white and is apparently changed to normal silver."

**Alloys of Silver.**—For practical use, as in making coins and silver-ware, an alloy with copper is used, the pure metal being too soft. The alloy usually contains from $7\frac{1}{2}$ to 10 per cent of copper. This alloy is harder than pure silver, and is capable of a higher polish. Silver

amalgam is an alloy of silver and mercury, which is readily formed by bringing the two metals together.

**Argentous Chloride, $Ag_2Cl$ or $Ag_4Cl_3$,** is formed by treating argentous salts with hydrochloric acid, and, possibly, to some extent when silver chloride, $AgCl$, is exposed to the light, though this is doubtful.

**Silver Chloride, Argentic Chloride, $AgCl$,** is of special importance on account of its use in photography and in chemical analysis. It occurs in nature to some extent in Mexico and in the United States. It is easily formed as a white precipitate by adding hydrochloric acid to a solution of a silver salt, as, for example, the nitrate. In consequence of its insolubility in water it affords a convenient means of detecting silver and chlorine. If allowed to stand in the light it changes color, becoming first violet and finally black. This change in color appears to be due entirely to the reduction of the chloride to the form of metallic silver. Concentrated hydrochloric acid dissolves it somewhat, and from this solution it crystallizes in octahedrons. An aqueous solution of ammonia dissolves it very easily, in consequence of the formation of a compound of the chloride with ammonia analogous to those formed by copper salts. The composition of the compound in the solution is, however, not known. Concentrated solutions of potassium, sodium, and ammonium chlorides dissolve silver chloride, forming double chlorides; and potassium cyanide also forms an easily soluble double salt with it. The dry compound absorbs ammonia gas, forming a compound of the formula $2AgCl.3NH_3$, which readily gives up the ammonia when gently heated.

**Silver Bromide, $AgBr$, and Silver Iodide, $AgI$,** are very similar to the chloride. Both occur in nature, and both are precipitated from solutions of silver salts by adding the corresponding hydrogen acids. The bromide is less easily soluble in ammonia than the chloride, and the iodide is almost insoluble in it. The bromide is formed by treating the chloride at the ordinary temperature with hydrobromic acid; and the iodide is formed from the chloride and from the bromide by treating these with

hydriodic acid at ordinary temperatures. At higher temperatures, however, both the bromide and iodide are converted into the chloride by hydrochloric acid. Silver dissolves in concentrated hydriodic acid, and from the solution a salt of the formula $AgI + HI$ or $HAgI_2$ is formed. It seems probable that this is a derivative of the acid $H_2I_2$, from which the double salt $KI.AgI$ is also derived, as indicated in the formula $KAgI_2$. Silver bromide at low temperatures is white, but easily changes to yellow, and by exposure it becomes darker, but not as readily as the chloride. The iodide is yellow, and undergoes change in the light only very slowly. The chloride and iodide exist in several modifications, which differ from one another in their conduct towards light, and in their solubility. Probably the differences are due to different complexity of the molecules. Modifications corresponding to the formulas $AgCl$, $AgI$, $Ag_2Cl_2$, $Ag_2I_2$, $Ag_3Cl_3$, $Ag_3I_3$, etc., are quite conceivable. The careful study of the effects of light upon the different modifications seems to promise interesting results, which may make it possible to judge as to the relative complexity of the molecules.

**Application of the Chloride, Bromide, and Iodide of Silver in the Art of Photography.**—The art of photography is based upon the changes which certain compounds, especially salts of silver, undergo when exposed to the light. Silver iodide is best adapted to most purposes. The salt is so changed by the light that when treated with certain compounds, such as ferrous sulphate, pyrogallic acid, etc., called "developers," a deposit of finely divided silver is formed upon the plate in those places affected by the light. A plate of glass or a sheet of properly prepared paper is covered in the dark with a thin layer of a salt of silver. The plate is then exposed in the camera to the action of the light which is reflected from the object to be photographed. According to the intensity of the light given off from the various parts of the object, the change of the silver salt takes place to a greater or less extent, and thus a perfect image of the object is impressed upon the plate. But after the action

of the "developer" is complete there is still upon the plate unchanged silver salt, and if this were now exposed to the light it would undergo change and the image would be obliterated. To remove this salt the plate is washed with a solution of sodium thiosulphate, $Na_2S_2O_3$ (hyposulphite), which dissolves the salt in consequence of the formation of a double salt of the formula $2Na_2S_2O_3.Ag_2S_2O_3$, which is readily soluble in water.

**Silver Triazoate, AgN₃.**—This is derived from triazoic acid (which see). It is formed by adding a solution of the acid to a solution of a silver salt. It is extremely explosive and should be dealt with very cautiously. Serious accidents have been caused by it. In appearance it resembles silver chloride, but it does not darken when exposed to the light.

**Silver Oxide, Ag₂O.**—The principal compound of silver and oxygen is that which has the composition $Ag_2O$, and in which the silver is univalent, as it is in its compounds with chlorine, bromine, and iodine. It is formed when a soluble hydroxide is added to a solution of a silver salt, and also by the action of concentrated solutions of the caustic alkalies on silver chloride. It is easily decomposed by heat and by reducing agents.

**Other Oxides of Silver.**—Besides the ordinary oxide, silver forms a sub-oxide, $Ag_4O$, corresponding to the sub-oxide of copper, $Cu_4O$, and a peroxide of the formula $AgO$ (or $Ag_4O_3$), which is perhaps analogous to cupric oxide.

**Sulphides of Silver.**—As has been stated, silver occurs in nature mostly in combination with sulphur as silver glance, $Ag_2S$, which is in many minerals in combination with other sulphides. Examples of such double sulphides are the minerals stromeyerite, $Cu_2S.Ag_2S$, and pyrargyrite, $3Ag_2S.Sb_2S_3$.

**Silver Nitrate, Argentic Nitrate, AgNO₃.**—This salt is formed by dissolving silver, or silver oxide, in nitric acid, evaporating to dryness, and heating until the salt is melted. It crystallizes in colorless rhombic plates. It is not changed in the light unless it comes in contact

with organic substances, when it is reduced and metallic silver deposited. Hence the solution produces black spots on the fingers and clothing. As it melts easily, it is generally cast in small cylindrical moulds, and is found in the market in the form of thin sticks, and is known as *lunar caustic*. It disintegrates flesh, and is used in surgery as a caustic to remove superfluous growths. Owing to the formation of a dark deposit when the salt is exposed to the light, it is used as a constituent of indelible inks. The dry nitrate absorbs ammonia and forms the compound $AgNO_3 + 3NH_3$; in concentrated solution the compound $AgNO_3 + 2NH_3$ is formed.

**Silver Cyanide, AgCN,** is formed as a caseous precipitate when a solution of hydrocyanic acid is added to a solution of silver nitrate. It does not change color in the light, is soluble in ammonia, but not in nitric acid. It readily forms double cyanides with the cyanides of other metals. Of these, the salt with potassium cyanide, $KAg(CN)_2$ or $KCN.AgCN$, may be mentioned.

**Silver Sulphocyanate, AgSCN,** is very similar to the cyanide, and is formed when solutions of silver nitrate and potassium or ammonium sulphocyanate are brought together. It is soluble in an excess of the soluble cyanides, double salts similar to the double cyanides being formed.

**Borates of Silver.**—When a cold concentrated solution of sodium metaborate, $NaBO_2$, is mixed with a similar solution of silver nitrate a precipitate of silver metaborate, $AgBO_2$, containing some silver oxide is formed. When dilute solutions of the two compounds are mixed a precipitate of silver oxide is formed; so, also, silver metaborate is decomposed by water into boric acid and silver oxide, and when the solution in which the precipitate is suspended is boiled the same change takes place. Further, when cold concentrated solutions of silver nitrate and borax are mixed, silver octoborate, $Ag_6B_8O_{15}$, is precipitated, and this is mixed with some silver oxide. When the solution is boiled, the silver salt is decomposed into boric acid and silver oxide. When

the solutions of borax and silver nitrate are mixed hot, the precipitate is the metaborate of silver.

**Reactions which are of Special Value in Chemical Analysis.**—*Hydrochloric acid* precipitates insoluble silver chloride from solutions of silver salts, as silver nitrate.

*Soluble hydroxides* precipitate silver oxide, not the hydroxide. Ammonia redissolves the precipitate in consequence of the formation of a compound of the oxide with ammonia of the composition $Ag_2O.2NH_3$. In dry condition this salt is very explosive, and is known as fulminating silver.

*Soluble carbonates* precipitate the carbonate, $Ag_2CO_3$, which has a yellowish-white color.

*Ammonium carbonate* redissolves the precipitate formed by it.

*Sodium phosphate*, $HNa_2PO_4$, gives a precipitate of the normal salt $Ag_3PO_4$, which is yellow.

*Potassium ferrocyanide* precipitates white silver ferrocyanide, $Ag_4Fe(CN)_6$.

*Potassium ferricyanide*, $K_3Fe(CN)_6$, gives the corresponding silver salt, which is reddish brown.

*Potassium chromate* or *potassium dichromate* (which see) gives a brownish-red precipitate of silver chromate.

### GOLD, Au (At. Wt. 195.74).

**General.**—Gold forms two series of compounds, in one of which it is univalent and in the other trivalent. In this respect it differs from the other members of the group. Examples of the compounds belonging to the two series are represented by the following formulas:

$$
\begin{array}{ll}
AuCl & AuCl_3 \\
AuBr & AuBr_3 \\
Au_2O & Au_2O_3
\end{array}
$$

Those of the first series are called *aurous compounds*, those of the second series *auric compounds*. The basic character of gold is very weak, so that salts of the ordinary acids, as sulphuric, nitric, carbonic, etc., are not

known. On the other hand, its higher oxide and hydroxide, $Au(OH)_3$, have acid properties, and form salts similar in composition to the meta-aluminates $MAlO_2$, and the metaborates $MBO_2$. These are the *aurates*, of which potassium aurate, $KAuO_2$, is an example. So, also, the chloride combines readily with the chlorides of potassium and sodium, forming the *chlor-aurates*, $KAuCl_4$, and $NaAuCl_4$, which are perfectly analogous to the aurates. Further, the chloride and bromide combine respectively with hydrochloric and hydrobromic acids, forming the crystallized compounds $HAuCl_4 + 4H_2O$ and $HAuBr_4 + 5H_2O$, which are plainly the acids from which the chlor-aurates and the brom-aurates are derived.

Besides the compounds of gold in which the element is univalent and those in which it is trivalent, the chloride $AuCl_2$, and the bromide, $AuBr_2$, have been described, but their existence is doubtful.

**Forms in which Gold occurs in Nature.**—Gold is generally found in nature in the native condition—a fact which is undoubtedly due to the chemical inactivity of the element. That which is found in nature is never pure, but contains silver, and also, in different localities, iron, copper, and other metals. It is also found to some extent in combination with tellurium in the compounds $AuTe_2$ and $(AuAg)_2Te_3$. Native gold is frequently found enclosed in quartz, or more commonly in quartz sand. The principal localities in which it is found are California and some of the other Western United States, and Australia, Hungary, Siberia, and Africa.

**Metallurgy of Gold.**—From the chemical point of view the metallurgy of gold is in general very simple. There are two kinds of gold mining—called *placer mining* and *vein mining*. In the former the earth and sand which contain gold are washed with water, which carries away the lighter particles, and leaves the gold mixed with other heavy materials. This mixture is then treated with mercury, which forms an amalgam with the gold, as it does with silver, and when this is placed in a properly constructed retort and heated, the mercury passes over and leaves the gold behind. If silver is present, as

is frequently the case, this is separated with the gold. In *vein mining* the gold ores are taken out of veins in the earth, and the gold separated by grinding the ores and treating them with mercury, as in the last stage of placer mining. *Hydraulic mining* is a modification of ordinary placer mining. It consists in forcing water under pressure against the sides of hills and mountains in which gold occurs loosely mixed with the earth. The earth is thus carried away and the heavier gold is deposited in sluices.

Some ores, those especially which contain tellurium, cannot be satisfactorily treated by the amalgamation process, and a method involving the use of potassium cyanide has been devised for them. In a solution of this salt gold dissolves, and from this solution it can be separated in various ways. This method has come into extensive use of late years.

Another process that is extensively used in the treatment of ores that do not give their gold to mercury is known as the *chlorination process.* This consists in treating the finely ground ore with chlorine made from bleaching powder and sulphuric acid, and then precipitating the gold from the solution of the chloride by means of hydrogen sulphide. From the sulphide the metallic gold can be easily obtained.

The gold obtained by any of the above methods is not pure. It can be separated from silver by dissolving it in *aqua regia*, evaporating so as to drive off the nitric acid, then diluting, and treating with a reducing agent, when metallic gold is precipitated. Thus when ferrous sulphate is used the following reaction takes place:

$$3FeSO_4 + AuCl_3 = Fe_2(SO_4)_3 + FeCl_3 + Au.$$

Another method of separating silver from an alloy with gold consists in treating the metal with nitric acid or with boiling concentrated sulphuric acid, which dissolves the silver and leaves the gold. This process is not satisfactory, however, unless the amount of gold in the alloy is less than 25 per cent. If the proportion of gold is greater than this, the alloy is melted with silver

enough to bring the percentage of gold down to that mentioned. This is known as "*quartation.*"

**Properties.**—Gold is a yellow metal with a high lustre. It is quite soft, and extremely malleable, so that it is possible to make from it sheets the thickness of which is not more than 0.000002 millimeter. Thin sheets are translucent, and the transmitted light appears green. Its specific gravity is 19.3; its melting-point higher than that of copper, being about 1200°. It crystallizes in the regular system. Gold combines directly with chlorine, but not with oxygen. The three acids, hydrochloric, nitric, and sulphuric, do not act upon it; but *aqua regia* dissolves it, forming auric chloride, $AuCl_3$, in consequence of the evolution of nascent chlorine. Molten caustic alkalies and their nitrates act upon it, probably in consequence of the tendency to form aurates.

**Alloys of Gold.**—The principal alloy of gold is that which contains copper. The standard gold coin of the United States contains nine parts of gold to one of copper. The composition of gold used for jewelry is usually stated in terms of carats. Pure gold is 24-carat gold; 20-carat gold contains 20 parts of gold and 4 parts of copper; 18-carat gold contains 18 parts of gold and 6 parts of copper, etc. Copper gives gold a reddish color, and makes it harder and more easily fusible. Gold is also alloyed with silver; and the alloy with mercury, known as gold-amalgam, is extensively used in the processes for extracting gold from its ores.

**Chlorides of Gold.**—When gold is dissolved in *aqua regia* it is converted into *auric chloride*, $AuCl_3$; and if this solution is evaporated a part of the chloride is decomposed into *aurous chloride*, $AuCl$, and chlorine. When gold is treated with dry chlorine it yields a mixture of auric chloride and metallic gold. This was formerly held to be a chloride of the formula $AuCl_2$, but the most careful investigations on the subject have shown that this does not exist. Auric chloride can be obtained in crystallized form, the crystals having the composition $AuCl_3 + 2H_2O$. When anhydrous auric chloride is heated to 185°, it loses chlorine and is converted into aurous chlo-

ride, AuCl. This yields auric chloride and gold when treated with water. When treated with a solution of stannous chloride a solution of auric chloride gives a purple-colored precipitate, known as the *purple of Cassius,* which appears to consist of finely-divided gold.

**Chlor-auric Acid and its Salts.**—When a solution of gold in *aqua regia* containing a large excess of hydrochloric acid is evaporated a crystallized product of the formula $HAuCl_4 + 4H_2O$, or $AuCl_3.HCl + 4H_2O$, is obtained. This is chlor-auric acid. It must be regarded as belonging to the same class as fluosilicic acid and the chloro-acids, from which the double chlorides of magnesium, aluminium, copper, etc., are derived. Accordingly its constitution is expressed by the formula

$$Au\!\!\begin{array}{l}\diagup Cl\\ -Cl\\ \diagdown (Cl_2)H\end{array}$$ , being similar to that of the acid from which

potassium chlor-aluminate is derived, $$Al\!\!\begin{array}{l}\diagup Cl\\ -Cl\\ \diagdown (Cl_2)H\end{array}$$ . The

potassium salt, $KAuCl_4$, is obtained by mixing together solutions of auric and potassium chlorides.

**Cyan-auric Acid, $HAu(CN)_4$,** is perfectly analogous to chlor-auric acid. It is formed by treating the potassium salt, $KAu(CN)_4$, with silver nitrate, which gives the silver salt, and then decomposing this with hydrochloric acid. The potassium salt is obtained by mixing solutions of auric chloride and potassium cyanide. The salts of a *cyan-aurous acid,* $HAu(CN)_2$, are also known.

**Auric Hydroxide, $Au(OH)_3$.**—This compound is formed by treating a solution of auric chloride with an excess of magnesia or with sodium hydroxide, and afterwards with sodium sulphate. It is a yellow or brown powder. When exposed to the light it is decomposed with evolution of oxygen. When heated to 100° it yields *auric oxide,* $Au_2O_3$, and when this is heated to a higher temperature it loses all its oxygen. *Aurous oxide,* $Au_2O$, is formed by treating aurous chloride with caustic potash. It is easily decomposed by heat into gold and oxygen.

Auric hydroxide dissolves in the soluble hydroxides just as aluminium hydroxide does, and from the solutions

salts known as the *aurates* are obtained. In composition these are analogous to the meta-aluminates. Potassium aurate, for example, has the composition $KAuO_2$. The analogy between some of the compounds of aluminium and those of gold is shown in the following table:

$$Al_2O_3 \qquad\qquad Au_2O_3$$
$$Al(OH)_3 \qquad\qquad Au(OH)_3$$
$$Al{<}^{O}_{OK} \qquad\qquad Au{<}^{O}_{OK}$$

$$AlCl_3 \qquad\qquad AuCl_3$$
$$Al{\Big\langle}{}^{Cl}_{-Cl}_{(Cl_2)K} \qquad\qquad Au{\Big\langle}{}^{Cl}_{-Cl}_{(Cl_2)K}$$

**Gold Sulphide, $Au_2S_3$.**—This compound is precipitated together with sulphur from cold solutions of gold salts by means of hydrogen sulphide, and forms a brownish black mass. It forms soluble compounds with the sulphides of the alkali metals.

When hydrogen sulphide is passed into hot solutions of gold salts aurous sulphide, $Au_2S$, is thrown down as a steel-gray substance. This is soluble in pure water and is reprecipitated by hydrochloric acid.

# CHAPTER XXIX.

**General.**—There is a very strong resemblance between the first two elements of this group and magnesium, while mercury, in a general way, resembles the first two members of the copper group. Just as gold in the copper group furnishes a greater variety of compounds than the first two members of that group, so mercury furnishes a greater variety of compounds than the other members of the group to which it belongs. Zinc and cadmium, like magnesium, give only one class of compounds and in these they are bivalent. The general formulas of some of the principal ones are:

$$MCl_2, \quad M(OH)_2, \quad MO, \quad MSO_4, \quad MCO_3, \quad MS.$$

Mercury, on the other hand, furnishes two series of compounds, known as the *mercurous* and *mercuric* compounds, which correspond closely to the two series of copper salts. The power to form compounds belonging to both series is more strongly developed in mercury than in copper. Examples of the two classes are represented in the following formulas:

| Mercurous Compounds. | Mercuric Compounds. |
|---|---|
| $HgCl$ | $HgCl_2$ |
| $HgI$ | $HgI_2$ |
| $Hg_2O$ | $HgO$ |
| $HgNO_3$ | $Hg(NO_3)_2,$ etc. |

Just as the first member of Group A, Family II, glucinum, shows a somewhat acidic character in its hydroxide, while the other members of that group do not; so also the first member of Group B, Family II, zinc, is

acidic, while the other members of the group are not. Glucinum hydroxide and zinc hydroxide dissolve in caustic alkalies, forming glucinates and zincates; while the hydroxides of all the other members of the two groups of this family are insoluble in caustic alkalies.

## ZINC, Zn (At. Wt. 64.91).

**General.**—Zinc, in almost all its compounds, exhibits a close resemblance to magnesium. It always acts as a bivalent element.

**Forms in which it occurs in Nature.**—Zinc occurs in nature in combination principally as the carbonate, or smithsonite, $ZnCO_3$; as the sulphide, or sphalerite, $ZnS$; and as the silicate, $Zn_2SiO_4$. Among other compounds of zinc found in nature are gahnite, $Zn(AlO_2)_2$, and franklinite, which contains the compound $Zn(FeO_2)_2$ with $Fe(FeO_2)_2$.

**Metallurgy.**—The metallurgy of zinc is much simpler than that of magnesium, for the reason that the ores are easily converted into the oxide by roasting, and the oxide is easily reduced by heating it with charcoal. Owing to the volatility of the metal the vessels in which the reduction is effected must be so constructed as to facilitate the condensation of the vapors. The vessels used are either earthenware muffles or tubes, open at one end and connected with iron receivers. At first the zinc vapor is condensed in the form of a fine dust, as in the case of sulphur. This forms the commercial product called *zinc dust.* It always contains zinc oxide. Afterwards the zinc condenses to the form of a liquid, and this is cast in plates. The zinc thus obtained is not pure, but contains lead and iron, and sometimes arsenic and cadmium. It is called *spelter.* By repeated distillation it can be obtained pure. When distilled under diminished pressure, it is deposited in beautiful lustrous crystals, the forms of which are extremely complicated.

**Properties.**—Zinc has a bluish-white color and a high lustre. The crystals above referred to, which are perfectly pure zinc, have a brilliant lustre, and do not

change in the air. At different temperatures zinc has markedly different properties. At ordinary temperatures it is quite brittle; at $100°–150°$ it can be rolled out in sheets, but above $200°$ it becomes brittle again. It melts at $433°$, and boils at $1040°$. When heated in the air it takes fire, and burns with a bluish flame, forming zinc oxide. This can be shown by means of the oxyhydrogen blowpipe. In dry air it does not change. Ordinary zinc dissolves in all the common acids, usually with evolution of hydrogen. In the case of nitric acid, however, the hydrogen acts upon the acid, reducing it to ammonia. The purer the zinc the less readily is it acted upon by sulphuric acid, and the pure crystals above referred to are scarcely acted upon at all by this acid. Zinc also dissolves in the caustic alkalies, forming zincates. Pure zinc can be made to act upon sulphuric acid by adding a few drops of platinum chloride.

**Applications.**—Zinc is extensively used as sheet-zinc, in making galvanic batteries, for galvanizing iron, etc. Zinc dust is a very efficient reducing agent, either in alkaline or in acid solution. With caustic alkalies—as, for example, with potassium hydroxide—it gives hydrogen and a zincate:

$$Zn + 2KOH = Zn(OK)_2 + H_2.$$

With sulphuric acid also it gives hydrogen readily. Zinc is used in the preparation of important alloys.

**Alloys.**—Iron covered with a layer of zinc is known as *galvanized iron*. As has been mentioned, zinc is a constituent of *brass*. It combines readily with mercury to form zinc amalgam, and this fact is taken advantage of for the purpose of preserving the zinc plates in galvanic batteries. Zinc plates covered with a layer of the amalgam are acted upon much more slowly than zinc itself. The amalgamation is effected by cleaning the zinc, dipping it in dilute sulphuric acid, and rubbing mercury over the surface with a brush or a piece of cloth.

**Zinc Chloride, $ZnCl_2$.**—This is prepared by treating zinc with chlorine, or by dissolving zinc in hydrochloric

acid, evaporating to dryness, and distilling the residue. It is a white deliquescent mass. From a very concentrated solution in hydrochloric acid it is obtained in crystals of the composition $ZnCl_2 + H_2O$. When the solution is evaporated there is always some decomposition into basic chlorides, the hydroxide, and oxide. The basic chloride is formed thus:

$$Zn<^{Cl}_{Cl} + HHO = Zn<^{OH}_{Cl} + HCl;$$

the hydroxide thus:

$$Zn<^{OH}_{Cl} + HHO = Zn<^{OH}_{OH} + HCl;$$

and by higher heating the hydroxide yields the oxide and water:

$$Zn<^{OH}_{OH} = ZnO + H_2O.$$

The chloride has a marked affinity for water, and is used in the laboratory, as sulphuric acid and phosphorus pentoxide are, for the purpose of extracting the elements of water from compounds. It has a caustic action, and is used in surgery on this account. Further, it acts as a disinfectant, and its solution is used for the purpose of preserving wood, particularly railroad sleepers, from decay.

The chloride readily forms double chlorides like those formed by magnesium chloride. Examples of these are the compounds of the formulas $ZnCl_2.2KCl$ or $K_2ZnCl_4$, $ZnCl_2.2NaCl$ or $Na_2ZnCl_4$, etc. The double chloride with ammonium chloride, $(NH_4)_2ZnCl_4$, is formed by mixing a solution of zinc in hydrochloric acid with a solution of ammonium chloride. This is used in soldering, as it cleans the surface of the metal, in consequence of the action of the zinc chloride on the oxides. It also absorbs ammonia, forming compounds analogous to those formed by cupric and cuprous chlorides.

**Zinc Hydroxide, $Zn(OH)_2$,** is precipitated as a white amorphous powder when a soluble hydroxide is added to a solution of a zinc salt. It is redissolved in an ex-

cess of the reagent, and the zincate thus formed is decomposed on boiling, the hydroxide being reprecipitated.

**Zinc Oxide, ZnO,** is formed in very finely divided condition by burning zinc in the air. The product is known as *Flores zinci*, and is sometimes called philosopher's wool. It is also formed by heating the carbonate or nitrate, and is found in nature mixed with or in combination with oxide of manganese, $Mn_3O_4$. It is prepared on the large scale both by burning zinc and by heating the basic carbonate, which is formed by adding sodium carbonate to a solution of zinc sulphate. It is a white powder, which turns yellow when heated. Its chief use is as a constituent of paint under the name of *zinc white*.

**Zinc Sulphide, ZnS.**—This compound occurs in nature, and is known as zinc blende. The mineral always contains a sulphide of iron, and also a small quantity of cadmium sulphide. When hydrogen sulphide is passed into a solution of a zinc salt only a part of the zinc is thrown down as the sulphide, if the salt used is one of a strong acid, like sulphuric, nitric, or hydrochloric acid. The reason of this is that the sulphide is soluble in these acids, even when they are very dilute. In the reaction the acid is set free, and although some sulphide is thrown down, the action soon stops:

$$ZnSO_4 + H_2S = ZnS + H_2SO_4.$$

If the acetate of zinc is used the precipitation is complete, because dilute acetic acid does not dissolve zinc sulphide. If sodium or potassium acetate is added to a solution of a neutral salt of zinc, hydrogen sulphide precipitates all the zinc, for the reason that the acid which is first set free acts upon the acetate and is itself neutralized, while acetic acid is then set free. Thus, when hydrogen sulphide acts upon a solution of zinc sulphate containing sodium acetate the action involves two steps, as represented in the two equations:

$$ZnSO_4 + H_2S = ZnS + H_2SO_4;$$
$$2NaC_2H_3O_2 + H_2SO_4 = Na_2SO_4 + 2C_2H_4O_2.$$

As fast as the sulphuric acid is formed it acts upon the acetate, and is thus prevented from dissolving the sulphide.

The sulphide is, further, completely precipitated by soluble sulphides, as potassium and ammonium sulphides. Obtained by precipitation, zinc sulphide is a white amorphous substance.

**Zinc Sulphate, ZnSO₄.**—This salt is readily formed by oxidation of the sulphide, and is hence found in nature accompanying the sulphide. It is manufactured by carefully roasting zinc blende, and extracting with water. It crystallizes from the solution in water in large rhombic prisms of the composition $ZnSO_4 + 7H_2O$. Like magnesium sulphate, it easily loses six molecules of water, but the last one is removed with difficulty. It appears, therefore, that the constitution of the salt should be expressed by the formula $SO\begin{cases} OH \\ OH \\ O \\ O \end{cases}>Zn$ . Zinc sulphate, as

has been stated (see p. 596), is commonly called white vitriol. It is easily reduced when heated with charcoal. The salt is used extensively in the preparation of cotton-prints and in medicine.

**Zinc Carbonate, ZnCO₃,** occurs in nature as smithsonite. The precipitate formed by adding a solution of a soluble carbonate to a solution of a zinc salt is generally a basic carbonate, but the composition varies according to the conditions. Dilute solutions of sodium carbonate and zinc sulphate give mainly the compound $\begin{matrix} Zn<{OH \atop O} \\ Zn<{O \atop O}>CO, \\ Zn<{O \atop OH} \end{matrix}$

or $Zn(OH)_2.ZnCO_3.ZnO$. Much more complicated salts are, however, usually obtained. With ammonia, zinc carbonate forms a soluble compound.

**Reactions which are of Special Value in Chemical Analysis.**—The principal reactions which are made use of for the purpose of separating zinc from other elements have been mentioned above. These are the reactions

with hydrogen sulphide and ammonium sulphide; with potassium and sodium hydroxide; with potassium and sodium carbonates; and with ammonium carbonate. Another reaction which is used in analysis is that which takes place when zinc salts are heated on charcoal before the blowpipe, moistened with cobalt nitrate, and ignited. Under these circumstances a green-colored mass known as Rinmann's green is formed, which is probably a zincate of cobalt, $Zn < {O \atop O} > Co$.

## Cadmium, Cd (At. Wt. 111.10).

**General.**—The compounds of cadmium are very similar to those of zinc and magnesium. The element occurs in nature in much smaller quantity than either of these, frequently in company with zinc, and its compounds are not as frequently met with. It is always bivalent. A mineral known as greenockite is cadmium sulphide, CdS.

**Preparation and Properties.**—Cadmium is obtained principally from different varieties of zinc blende, and separates with the zinc. Being more volatile than zinc, it passes over first when the mixture is distilled. From this first distillate, which contains the oxides of zinc and cadmium, the metals are reduced by heating with charcoal. It has a color like that of tin, and is harder than tin. According to the specific gravity of its vapor, its molecule is identical with its atom, for the molecular weight is approximately 111.

*Cadmium chloride*, $CdCl_2$, like zinc chloride, is volatile; the *sulphate* crystallizes well, but is not analogous in composition to the sulphates of magnesium and zinc, as the composition of the crystallized salt is represented by the formula $3CdSO_4 + 8H_2O$; the *normal carbonate*, $CdCO_3$, is precipitated by soluble carbonates.

**Cadmium Sulphide, CdS,** is one of the most characteristic compounds of the element. It is a beautiful yellow substance, which is thrown down from a solution of a cadmium salt by hydrogen sulphide. While it dissolves

in concentrated acids it does not dissolve in dilute acids, and it is therefore completely precipitated by hydrogen sulphide. It is used as a constituent of yellow paints.

**Cadmium Cyanide, Cd(CN)₂**, is formed as a white precipitate when potassium cyanide is added to a fairly concentrated solution of a cadmium salt. It dissolves in an excess of potassium cyanide in consequence of the formation of the compound $K_2Cd(CN)_4$.

**Analytical Reactions.** — Cadmium, as has just been stated, is precipitated by hydrogen sulphide. It is thrown down together with the other elements of the hydrogen sulphide group (see p. 198). As the sulphide is not soluble in ammonium sulphide, it is easily separated from those of arsenic, antimony, and tin by treating with this reagent, when it is left undissolved in company with the sulphides of mercury, lead, bismuth, and copper. The double salt of cuprous cyanide and potassium cyanide is not decomposed by hydrogen sulphide, whereas the corresponding salt of cadmium is decomposed by it, and the yellow sulphide is precipitated.

The hydroxide of cadmium differs from that of zinc in not having acid properties. It does not dissolve in the caustic alkalies.

## MERCURY, Hg (At. Wt. 198.49).

**General.**—As already stated, mercury yields two series of compounds, known as mercurous and mercuric compounds, which are analogous to the two series of copper compounds. While, however, copper forms with the oxygen acids only such salts as belong to the cupric series, as $CuSO_4$, $Cu(NO_3)_2$, etc., mercury forms salts belonging to both series. There is, for example, a *mercurous nitrate*, $HgNO_3$, and a *mercuric nitrate*, $Hg(NO_3)_2$; a *mercurous sulphate*, $Hg_2SO_4$, and a *mercuric sulphate*, $HgSO_4$, etc. The mercurous compounds are readily converted into the mercuric compounds by the action of oxidizing agents, and the mercuric are converted into mercurous compounds by the action of reducing agents. The action will be treated of under the individual compounds. The question as to the correct formula of the

mercurous salts is in the same condition as that in regard to the formula of cuprous salts, with this difference : the molecular weight of mercurous chloride leads to the formula HgCl, but there is evidence that when the chloride is heated some mercury is set free, and this has led to the suggestion that the molecule corresponds to the formula $Hg_2Cl_2$, and that the compound breaks down into mercury and mercuric chloride when heated. It is, however, quite possible that the compound has the simpler formula, and that this under the influence of heat is partly decomposed, as represented in the equation

$$2HgCl = HgCl_2 + Hg.$$

The fact that mercury is set free is, therefore, by no means satisfactory evidence that the formula of mercurous chloride is $Hg_2Cl_2$, and in the present state of the inquiry it is perfectly justifiable to write the formula HgCl.

**Forms in which Mercury occurs in Nature.**—Mercury occurs native to some extent, but principally in the form of the sulphide, HgS, which is known as cinnabar. This is sometimes found crystallized, but generally amorphous. The chief localities are Idria, Almaden in Spain, and New Almaden in California.

**Metallurgy of Mercury.**—In order to obtain mercury from the sulphide this is roasted in vessels so constructed as to condense and collect the vapor of mercury given off. In the roasting process the sulphur is oxidized to sulphur dioxide, which of course escapes. In some places the ore is mixed with limestone and distilled from clay or iron retorts, when the mercury passes over. Crude mercury is redistilled in order to purify it. It is also purified by treating it with dilute nitric acid or with a solution of ferric chloride.

**Properties.**—Mercury is a silver-white metal of a high lustre. At ordinary temperatures it is liquid, though at —39.5° it becomes solid. Its specific gravity is 13.5959. It does not change in the air at ordinary temperatures. It boils at 357.25°, and is converted into a colorless vapor, the specific gravity of which leads to the conclusion that,

as in the case of cadmium, the molecule and atom are identical, or that the molecule consists of only one atom. It is insoluble in hydrochloric acid and in cold sulphuric acid ; but dissolves in hot concentrated sulphuric acid, and is easily soluble in nitric acid. The vapor of mercury is very poisonous.

**Applications.** — Mercury is extensively used in the manufacture of thermometers, barometers, etc. ; as tin-amalgam for mirrors ; and in the processes by which gold and silver are obtained from their ores.

**Amalgams.**—The alloys which mercury forms with other metals are called amalgams. These compounds are generally obtained without difficulty simply by bringing mercury in contact with other metals. Among the amalgams which are of chief interest are those of sodium, ammonium, silver, and gold. *Sodium amalgam* is made by bringing mercury and sodium together. A crystallized amalgam containing the constituents in the proportions represented in the formula $Hg_6Na$ has been obtained. Generally, sodium amalgam is easily decomposed by water, the mercury separating in the free state and the sodium acting upon the water, forming hydrogen and sodium hydroxide. It is much used in the laboratory as a convenient means of producing hydrogen in alkaline solutions. It serves as an excellent reducing agent in some cases. *Ammonium amalgam* has already been spoken of under the head of Ammonia (which see). It is a curious substance, which is formed when an electric current acts upon a solution of ammonia containing some mercury which is connected with the negative pole, and also very easily by pouring a solution of ammonium chloride upon sodium amalgam. In the latter case sodium chloride and ammonium amalgam are formed. Apparently the reaction takes place in accordance with the following equation :

$$NH_4Cl + NaHg = NaCl + NH_4Hg.$$

The product is extremely voluminous, and swells up during the reaction, so that it occupies under favorable

circumstances about twenty times the volume occupied by the sodium amalgam. It has a metallic lustre, resembling in general the other amalgams. It is very unstable at the ordinary temperature, breaking down into mercury, hydrogen, and ammonia. At a low temperature, however, it has been obtained in crystallized form. The metallic lustre and general outward appearance of the compound suggests that whatever is in combination with mercury in it has probably metallic properties, and this affords some confirmation of the ammonium theory, according to which the presence of the complex, $NH_4$, in the salts formed by ammonia is assumed. *Silver amalgam* and *gold amalgam* vary in composition according to the method of preparation, and when heated are comparatively easily decomposed.

**Mercurous Chloride, HgCl,** is commonly called calomel. Like cuprous chloride, CuCl, and argentic chloride, AgCl, it is insoluble in water. It is formed most readily by reducing mercuric chloride. The reduction can be accomplished by means of sulphurous acid, when the following reaction takes place :

$$2HgCl_2 + 2H_2O + SO_2 = 2HgCl + H_2SO_4 + 2HCl.$$

It is also formed by heating together mercuric chloride and mercury, and by subliming a mixture of mercuric sulphate, sodium chloride, and mercury. This method is the one mostly used in the manufacture of calomel. The product obtained by sublimation is crystalline ; the precipitated substance forms a loose powder. As was stated above, the specific gravity of the vapor corresponds to that required for the formula HgCl. When acted upon for some time by light it undergoes partial decomposition into mercury and mercuric chloride. This is a fact of great importance, inasmuch as calomel is much used in medicine, and mercuric chloride is an active poison. Bottles in which calomel is kept should be carefully protected from the action of the light.

Just as mercuric chloride is converted into mercurous chloride by reducing agents, so the latter is converted into the former by oxidizing agents. When, for example,

mercurous chloride is treated with nitric acid it is converted into mercuric chloride and mercuric nitrate, as represented in the equation

$$6HgCl + 8HNO_3 = 3Hg(NO_3)_2 + 3HgCl_2 + 2NO + 4H_2O.$$

If hydrochloric acid is present in sufficient quantity the action takes place thus:

$$3HgCl + 3HCl + HNO_3 = 3HgCl_2 + 2H_2O + NO.$$

Further, the conversion of mercurous nitrate into mercuric nitrate is represented by the equation

$$3HgNO_3 + 4HNO_3 = 3Hg(NO_3)_2 + 2H_2O + NO.$$

Finally, the action of oxidizing agents in general upon mercurous chloride in the presence of hydrochloric acid takes place thus:

$$2HgCl + 2HCl + O = 2HgCl_2 + H_2O.$$

Similar transformations take place by treating ferrous, stannous, and manganous compounds with oxidizing agents; and they will be taken up farther on.

**Mercuric Chloride,** or **Corrosive Sublimate, $HgCl_2$,** which is made by subliming a mixture of sodium chloride and mercuric sulphate,

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4,$$

and by dissolving mercury in *aqua regia*, evaporating to dryness, and subliming the residue, is a white, transparent, crystalline mass, which is soluble in water, and can be obtained in crystalline form from the solution. It is more easily soluble in alcohol and ether than in water, and is extracted from a water solution by shaking with ether. It is quite volatile, and the specific gravity of its vapor corresponds to that required for the formula $HgCl_2$. It is easily reduced to mercurous chloride by

contact with organic substances, and by reducing agents in general. The action of sulphur dioxide has already been treated of as furnishing a method for the preparation of mercurous chloride. Stannous chloride abstracts chlorine from it and forms mercurous chloride and metallic mercury, while the stannous chloride is converted into stannic chloride :

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4 \, ;$$
$$HgCl_2 + SnCl_2 = Hg \quad + SnCl_4.$$

Mercuric chloride is an active poison, and has been used extensively in this capacity. It has a very marked influence upon the lower organisms, which play such an important part in producing disease and the decay of organic substances, and is used as a disinfectant. Wood impregnated with a solution of it is partly protected from decay. In surgery it is used for the purpose of preventing contamination of wounds by the hands and instruments of the surgeon, it being customary now for the surgeon to wash his hands and instruments in a dilute solution of the chloride before performing an operation.

Mercuric chloride unites with other chlorides, forming well-characterized double chlorides, or *chlor-mercurates*, which are analogous to the double chlorides of magnesium, zinc, etc. Three potassium salts are known, $KHgCl_3$, $K_2HgCl_4$, and $KHg_2Cl_5$; or $Hg{<}^{Cl}_{Cl_2K}$, $Hg{<}^{Cl_2K}_{Cl_2K}$, and $Hg{<}^{Cl}_{Cl_2} \, Hg{<}^{Cl_2}_{(Cl_2)K}$. Similar salts are formed with the chlorides of sodium, ammonium, calcium, barium, strontium, and other metals. Further, hydrochloric acid forms, with mercuric chloride, a crystallized compound of the formula $HHg_2Cl_5$ or $2HgCl_2.HCl$, which is plainly the acid from which the potassium salt $KHg_2Cl_5$ is derived.

**Mercurous Iodide, HgI,** can be made by treating mercury with iodine ; or by treating mercuric iodide with mercury ; and more easily by adding potassium iodide to a solution of a mercurous salt, when it is thrown down

as a greenish-yellow powder. It is unstable, and breaks down, yielding mercury and mercuric iodide. When treated with potassium iodide it suffers the same decomposition, the iodide which is formed combining with the potassium iodide, while mercury is deposited. Mercurous iodide is used in medicine. As it is more easily decomposed than mercurous chloride, and mercuric iodide is poisonous, care should be taken in its use.

**Mercuric Iodide,** $HgI_2$, is made by direct combination of mercury and iodine, and by the action of potassium iodide upon a solution of a mercuric salt, when it is precipitated as a beautiful scarlet-red powder. Though insoluble in water, it is soluble in alcohol and ether. It dissolves, further, in a solution of potassium iodide in consequence of the formation of a double iodide, or iodo-mercurate. When heated to about 150° the color changes from red to yellow, and after cooling the yellow substance changes to red. Sometimes it can be kept in the condition in which it has a yellow color for some time after it has cooled down, and then if touched at one point the change to the red substance takes place rapidly through the entire mass. Both the red and the yellow modifications are crystallized, but in different forms. The red crystals are tetragonal; the yellow ones are rhombic or monoclinic. The monoclinic structure is evidently, from what has been said, an unstable one for this compound. It seems probable that the difference between the two forms is due to a difference in the complexity of the molecules; perhaps the larger molecules of the red iodide are decomposed by heat into the smaller molecules of the yellow iodide. When the iodide is first precipitated from a solution of mercuric chloride by potassium iodide it is yellow, but it rapidly turns red.

Just as mercuric chloride forms a compound with hydrochloric acid, so mercuric iodide forms similar compounds. These have the composition represented by the formulas $HgI_2.HI$ or $HHgI_3$, and $2HgI_2.3HI$ or $H_3Hg_2I_7$. It also combines with iodine, forming the periodide $HgI_3$, which is decomposed by water, forming mercuric iodide. With potassium chloride it forms the salts

$K_2HgI_4$ or $HgI_2.2KI$, and $KHgI_3$ or $HgI_2.KI$. These salts form colorless solutions. They are also formed by the action of potassium iodide upon mercurous iodide, when mercury separates:

$$2HgI + 2KI = K_2HgI_4 + Hg.$$

Similar double iodides are formed with the chlorides of sodium, ammonium, barium, calcium, strontium, magnesium, and other metals.

**Mercurous Oxide, $Hg_2O$,** is formed by treating a mercurous salt with potassium hydroxide. It is a black powder, and decomposes easily into mercuric oxide and mercury when the light shines upon it.

**Mercuric Oxide, $HgO$,** like the iodide, presents itself in two colors—the red and the yellow. When mercury is heated for a long time at a temperature near the boiling-point so that the air has access to it, it is converted into the red oxide. When a solution of a mercuric salt is treated with caustic soda or caustic potash the yellow oxide is precipitated. When heated, the red oxide becomes darker, and finally nearly black, and on cooling the red color reappears. The yellow oxide also becomes darker on heating. Exposed to the light, the red oxide loses some of its oxygen, and mercury is deposited. When heated to a sufficiently high temperature both varieties give up all their oxygen, as was seen in the case of the red oxide in the preparation of oxygen. It will be remembered that oxygen was discovered by heating this compound. Of what overwhelming importance this discovery was the student will now better appreciate than when the discovery was first mentioned. It will now be seen that most of the chemical phenomena with which we have to deal involve the action of oxygen.

Hydroxides of mercury are not known.

**Mercurous Sulphide, $Hg_2S$.**—There seems to be some question whether a compound of the formula $Hg_2S$ exists or not. According to the latest investigations on the subject, the precipitate which is formed when hydrogen sulphide is passed into a solution of a mer-

curous salt is a mixture of mercuric sulphide, HgS, and mercury. At all events, it is certain that, even if mercurous sulphide exists, it breaks down with great ease into the mercuric compound and mercury.

**Mercuric Sulphide, HgS,** is the principal compound of mercury found in nature. This natural variety, which is known as cinnabar, is a red crystallized compound. When prepared by treating a solution of a mercuric salt with hydrogen sulphide it is an amorphous black powder. This black powder can, however, be converted into the red crystallized variety by sublimation, and by allowing it to stand in contact with a solution of the sulphide of an alkali metal. The sulphide, whether amorphous or crystallized, is acted upon with difficulty by acids. Dilute nitric acid, which easily dissolves the sulphides of the other metals which resemble mercury, leaves it unacted upon, and advantage is taken of this fact for the purpose of separating it from the sulphides of lead, bismuth, copper, and cadmium in qualitative analysis. It is dissolved by concentrated nitric acid and by aqua regia. In the former case a white insoluble compound of mercuric nitrate and mercuric sulphide, $Hg(NO_3)_2.2HgS$, is sometimes formed. Potassium hydrosulphide dissolves mercuric sulphide, forming a compound, $K_2HgS_2$, or $K_2S.HgS$, which is easily decomposed by water, mercuric sulphide being thrown down. The substance used in medicine under the name *Ethiops martialis* is an intimate mixture of amorphous sulphide and sulphur. Like the oxide, cinnabar turns dark when heated, and it slowly undergoes the same change when exposed to the light, in consequence of a slight decomposition into mercury and sulphur. When that which has not been heated to too high a temperature is cooled down again, it acquires its original red color. If it has been heated to the temperature of sublimation, the black color of that which does not sublime is permanent. Cinnabar is used as a pigment in the manufacture of red paints.

**Mercuric Cyanide, $Hg(CN)_2$,** is formed by dissolving mercuric oxide in an aqueous solution of hydrocyanic

acid. It is soluble in water, and crystallizes well in quadratic prisms. When heated it is decomposed into cyanogen and mercury, and this affords the most convenient method of making cyanogen. When heated rapidly there is formed a considerable quantity of a black substance called *paracyanogen,* which has the same percentage composition as cyanogen, but is not volatile. This is probably a polymeric variety of cyanogen. The cyanide unites with the cyanides of other metals, forming double cyanides, of which those corresponding to the following formulas are good examples: $K_2Hg(CN)_4$, $MgHg(CN)_4$, etc. These are soluble in water, and, as a rule, crystallize well.

*Fulminating mercury* is an explosive compound much used in the manufacture of gun-caps. It is made by dissolving mercury in nitric acid and adding alcohol. Its explosion consists in a sudden breaking down into nitrogen, carbon dioxide, and mercury. The composition of the compound is represented by the formula $C_2N_2O_2Hg$. It would lead too far to discuss its constitution—a subject which has occupied the attention of some of the most celebrated chemists.

**Mercurous Nitrate, $HgNO_3$,** is made by treating nitric acid with an excess of mercury. This salt is easily decomposed, forming difficultly soluble basic salts, some of which are of complicated composition. The simplest is that which has the composition $HgOH.HgNO_3$. This is easily explained on the assumption that the nitrate has the formula $\begin{matrix} Hg(NO_3) \\ | \\ Hg(NO_3). \end{matrix}$ The decomposition by water is then represented by the equation

$$\begin{matrix} Hg(NO_3) \\ | \\ Hg(NO_3) \end{matrix} + H_2O = \begin{matrix} Hg(NO_3) \\ | \\ Hg(OH) \end{matrix} + HNO_3.$$

This may possibly be regarded as a slight argument in favor of the doubled formula for the mercurous compound. It is, however, far from conclusive, as the salt may be considered to be made up as represented in this

formula, $ON \begin{cases} OH \\ OHg \\ OHg \end{cases}$, according to which it is a derivative

of the acid $NO(OH)_3$, corresponding to phosphoric acid, $PO(OH)_3$.

**Mercuric Nitrate, $Hg(NO_3)_2$,** is formed by treating mercuric oxide with an excess of nitric acid and evaporating, when the salt can, under favorable circumstances, be obtained in crystals. It is easily decomposed by water, with formation of a basic salt which is insoluble in water. It has the composition represented by the formula $NO_3-Hg-O-Hg-O-Hg-NO_3 + H_2O$.

**Compounds formed by Salts of Mercury with Ammonia.** —Attention has already been called to the compounds formed by the salts of copper with ammonia, and the statement was made that this power to combine with ammonia and with ammonium salts is very common among the salts. Some of these compounds which are formed by the salts of mercury are of special interest. When mercuric chloride is treated with ammonia a white precipitate is formed, the composition of which is represented by the formula $HgClNH_2$. The formation takes place according to the equation

$$HgCl_2 + 2NH_3 = HgClNH_2 + NH_4Cl.$$

The simplest view in regard to the constitution of this compound is that it is mercuric chloride in which a chlorine atom is replaced by the group $NH_2$, or *amide*, as represented in the formula $Hg{<}{Cl \atop NH_2}$. According to this view the compound is called *mercuric chloramide.* It is known as *white precipitate,* or, to distinguish it from another similar compound, as *infusible white precipitate.* It is also possible that the constitution of the compound should be represented by the formula $N \begin{cases} H_2 \\ Hg \\ Cl \end{cases}$, according

to which it is ammonium chloride in which two atoms of hydrogen are replaced by an atom of bivalent mercury. The similar compound referred to is formed by adding a solution of mercuric chloride to a boiling solution of am-

monium chloride containing ammonia, and separates out on cooling. It has the composition $Hg(NH_2Cl)_2$, and is to be regarded as ammonium chloride, in two molecules of which two hydrogen atoms are replaced by an atom of bivalent mercury, as represented in the formula $Hg < {H_2NCl \atop H_2NCl}$. This is called *mercuric diammonium chloride*, or *fusible white precipitate*. Mercurous compounds corresponding to both the above-mentioned derivatives of mercuric chloride are known. The first, or *mercurous chloramide*, $Hg_2NH_2Cl$, is the black substance formed when mercurous chloride is treated with ammonia:

$$2HgCl + 2NH_3 = Hg_2NH_2Cl + NH_4Cl.$$

The second, or *mercurous ammonium chloride*, $HgNH_3Cl$, is formed by treating calomel with ammonia gas.

Similar compounds are obtained from the other salts of mercury. In a solution of mercurous nitrate ammonia forms a black precipitate, known in pharmacy as *Mercurius solubilis Hahnemanni*. It may be regarded as derived from ammonium nitrate by replacement of two hydrogen atoms by two atoms of mercury, as represented in the formula $Hg_2H_2N.NO_3$.

**Reactions which are of Special Value in Chemical Analysis.**—As has been seen in the account already given of the conduct of the compounds of mercury, mercurous and mercuric compounds conduct themselves quite differently. Among the most characteristic reactions of *mercurous* compounds are the following:

*Sodium* or *potassium hydroxide* gives a black precipitate of mercurous oxide.

*Ammonia* gives a black precipitate which is a compound of mercurous oxide and ammonia.

*Hydrochloric acid* and *soluble chlorides* form mercurous chloride, and the precipitate turns black when treated with ammonia.

The reactions with stannous chloride, potassium iodide, hydrogen sulphide, and ammonium sulphide have been explained.

The principal reactions of the *mercuric* salts are the

following : *Sodium* or *potassium hydroxide* produces a yellow precipitate of mercuric oxide.

The reactions with hydrogen sulphide, stannous chloride, and potassium iodide have been described above.

### ELEMENTS OF FAMILY III, GROUP B:
### GALLIUM—INDIUM—THALLIUM.

**General.**—All the elements of this group are rare. Gallium forms compounds which in composition are analogous to those of aluminium, in which it is trivalent, as in the compounds $GaCl_3$, $Ga_2O_3$, $Ga(NO_3)_3$, $Ga_2(SO_4)_3$, etc. On the other hand, it also forms compounds in which it is bivalent, as in the chloride $GaCl_2$ and $GaO$. Indium also forms compounds in which it is trivalent, and a few in which it is bivalent. Thallium, like gold, is trivalent and univalent in its compounds.

**Gallium, Ga** (**At. Wt. 69.38**).—This element is found in some varieties of zinc blende, and was discovered in that which occurs at Pierrefitte, in France. It owes its name to the Latin name of France, Gallia. Like scandium, it is of special interest for the reason that its properties were foretold by Mendeléeff some years before it was discovered, and it was described by him under the name of eka-aluminium, as scandium was described under the name of eka-boron. The metal has a bluish-white color, and does not lose its lustre in the air. It does not decompose water. Even when heated to a high temperature in oxygen it only becomes covered with a thin layer of oxide. It dissolves in hydrochloric acid and in potassium hydroxide with evolution of hydrogen.

**Compounds of Gallium.**—The chlorides of gallium, $GaCl_2$ and $GaCl_3$, are formed by treating the metal with chlorine. With water both give basic chlorides. That formed from *gallous chloride*, $GaCl_2$, is completely converted into gallium oxide by further action of water. *Gallic sulphate*, $Ga_2(SO_4)_3$, is decomposed by boiling water, a basic salt being formed. With ammonium sulphate it forms a double sulphate of the formula $NH_4Ga(SO_4)_2 + 12H_2O$, which is perfectly analogous to ammonium alum (see Alums, p. 576).

**Indium, In (At. Wt. 112.99).**—Indium was discovered in a variety of zinc blende found at Freiberg, in Germany. The discovery was made by means of the spectroscope, and as the spectrum of the element contains two very characteristic blue lines it was called indium. It has since been found in other varieties of zinc blende, but always in small quantity. It is a soft, white, lustrous metal. It does not undergo change in contact with the air at ordinary temperatures, but when heated it takes fire and burns, forming the oxide. It does not decompose water even at the boiling temperature.

**Compounds of Indium.**—With chlorine indium forms the compound $InCl_3$, which is volatile at a high temperature. The specific gravity of the vapor is that required for the formula $InCl_3$. The *sulphate* is easily formed by dissolving the metal in sulphuric acid. It combines with ammonium sulphate to form the double sulphate $NH_4In(SO_4)_2 + 12H_2O$, analogous to alum. The corresponding potassium salt does not contain the same number of molecules of water of crystallization.

**Thallium, Tl (At. Wt. 202.61).**—This element was discovered in the flue-dust of a sulphuric-acid factory in the Harz mountains, by the aid of the spectroscope. As it colors the flame a beautiful green it was called thallium, from the Greek $\vartheta\alpha\lambda\lambda os$, which signifies a green branch. It has since been found in a number of varieties of iron pyrites and copper pyrites. It is a soft, bluish-white metal, and has a lustre like lead. It is oxidized when heated to a sufficiently high temperature in the air.

**Compounds of Thallium.**—When thallium is treated with chlorine it is converted into *thallous chloride*, TlCl; and when this is treated under water with chlorine it is converted into the trichloride or *thallic chloride*, $TlCl_3$. Thallous chloride, further, is formed as a caseous precipitate when hydrochloric acid is added to a solution of a thallous salt. When exposed to the light it turns violet. —*Thallous hydroxide*, Tl(OH), is formed by the action of the metal on water in the air, and by treating a solution of the sulphate with barium hydroxide. It is easily soluble in water, and the solution has an alkaline reac-

tion.—*Thallic hydroxide*, $Tl(OH)_3$, is formed by treating a solution of thallic chloride with potassium hydroxide. When dried it loses water and forms the compound $TlO.OH$, analogous to metaboric acid, $BO.OH$, and meta-aluminic acid, $AlO.OH$. Thallium forms an insoluble chloride, $TlCl$, which turns violet when exposed to the light, and in this respect it resembles silver; the formation of the soluble hydroxide, $Tl(OH)$, which has an alkaline reaction, is highly suggestive of the alkali metals; while the formation of the hydroxide, $TlO(OH)$, shows that thallium is allied to aluminium. An examination of its salts shows that those in which it is univalent resemble the salts of the alkali metals, while those in which it is trivalent resemble the salts of aluminium. —*Thallous sulphate*, $Tl_2SO_4$, and the *thallous phosphates*, $H_2TlPO_4$, $HTl_2PO_4$, and $Tl_3PO_4$, are isomorphous with the corresponding salts of potassium.—*Thallous sulphide* is thrown down as a black powder when hydrogen sulphide is passed into a solution of a thallous salt.—*Thallic sulphate*, $Tl_2(SO_4)_3$, combines with sulphates of the alkali metals, forming salts of the general formula $TlM(SO_4)_2$; but these do not crystallize like the alums. On the other hand, thallous sulphate, $Tl_2SO_4$, combines with aluminium sulphate, and other similar sulphates, forming salts perfectly analogous to the alums, and in these the thallium takes the place of the alkali metal, as, for example, in the salts

$$TlAl(SO_4)_2 + 12H_2O, \quad TlFe(SO_4)_2 + 12H_2O, \quad \text{etc.}$$

# CHAPTER XXX.

**General.**—Of the elements of this group germanium is extremely **rare**. It was discovered by Winkler in 1885. Tin and lead, on the other hand, have long been known, and are extensively used. All form two series of compounds, in one of which they are bivalent and in the other quadrivalent. The general formulas of some of the principal compounds of the first series are as follows:

$$MCl_2, \ MO, \ M(OH)_2, \ M(NO_3)_2, \ MSO_4, \ MCO_3, \ etc.$$

The general formulas of some of the principal compounds of the other series are as follows:

$$MCl_4, \ MO_2, \ M(OH)_4, \ MO(OH)_2, \ etc.$$

These elements have already been referred to at the close of Chapter XXII. (see p. 425), and attention was then called to the resemblance between them and carbon and silicon. In this connection it will be well to repeat what was there said. Of the three elements of the group, germanium and tin are more acidic in character than lead. They combine with chlorine in two proportions, forming the chlorides $GeCl_2$, $SnCl_2$, $PbCl_2$, $GeCl_4$, $SnCl_4$, $PbCl_4$. With oxygen they combine to form the compounds $GeO_2$, $SnO_2$, and $PbO_2$. Stannic oxide, $SnO_2$, and lead peroxide, $PbO_2$, form salts with bases, and these have the composition represented by the general formulas $M_2SnO_3$ and $M_2PbO_3$, and are therefore analogous to the silicates, carbonates, and titanates. On the other hand, further, salts are known which are derived from the oxide PbO. These have the general formula $M_2PbO_2$,

and are to be regarded as salts of an acid $Pb(OH)_2$. These salts are not stable, and are not easily obtained. Most of the derivatives of lead are those in which it plays the part of a base-forming element. Notwithstanding the marked analogy between some of the compounds of tin and those of the members of the silicon group, it appears, on the whole, advisable to treat of this element in company with lead, which it also resembles in many respects.

## GERMANIUM, Ge (At. Wt. 71.93).

Germanium is the third element the properties of which were foretold by Mendeléeff by the aid of the periodic law. As it occurs in the silicon group he called it *eka-silicon*. It was discovered in a silver ore occurring at Freiberg, Germany. The name has, of course, reference to the country in which it was discovered. It acts mostly as a base-forming element, being perhaps more like tin than any other one metal. It forms the two chlorides $GeCl_2$ and $GeCl_4$, and the corresponding fluorides $GeF_2$ and $GeF_4$; but preferably it forms those compounds in which the element is quadrivalent. The fluoride forms double salts resembling the fluosilicates, as, for example, *potassium fluogermanate*, $K_2GeF_6$.

## TIN, Sn (At. Wt. 118.15).

**General.**—The compounds of tin with which we generally have to deal belong, with the exception of stannous chloride, to the series in which the metal is quadrivalent, and in this series it acts as an acid-forming element. The chloride, $SnCl_4$, corresponds to the chlorides of carbon and silicon, $CCl_4$ and $SiCl_4$. Unlike these elements, however, it does not form a compound with hydrogen.

**Occurrence.**—Tin occurs almost exclusively as tin stone or cassiterite in nature. This is the dioxide, $SnO_2$, corresponding to carbon dioxide, $CO_2$; silicon dioxide, $SiO_2$; titanium dioxide, $TiO_2$; etc. It also occurs in small quantities in company with gold as metallic tin,

and in a variety of pyrites of the formula $Cu_4SnS_4 + FeSnS_4$, known as stannite.

**Metallurgy.**—The ores are roasted for the purpose of getting rid of the sulphur and arsenic, and the oxide is then heated with coal in a furnace. After the reduction is complete the tin is drawn off and cast in bars. This tin is impure, and when again slowly melted, that which first melts is purer. By letting it run off as soon as it melts the comparatively difficultly fusible alloy remains behind, and the tin is thus rendered much purer. The commercial variety of tin known as *Banca tin* is the purest. It receives its name from Banca, in the East Indies, where it is made. *Block-tin* is made in England, and is also comparatively pure.

**Properties.**—Tin is a white metal, which in general appearance resembles silver. It is soft and malleable, and can be hammered out into very thin sheets, forming the well-known tin-foil. Its specific gravity is 7.3. At 200° it is brittle, and at 228° it melts. At ordinary temperatures it remains unchanged in the air. It dissolves in hydrochloric acid, forming stannous chloride, $SnCl_2$; in sulphuric acid, forming stannous sulphate, $SnSO_4$, sulphur dioxide being evolved at the same time. Ordinary concentrated nitric acid oxidizes it, the product being a compound of tin, oxygen, and hydrogen, known as *metastannic acid*, which is a white powder insoluble in nitric acid and in water. It is dissolved by a hot solution of potassium hydroxide which forms potassium stannate, $K_2SnO_3$.

**Applications.**—It is used in making alloys, of which bronze (see p. 591), soft solder, and britannia metal are the most important. It is used also for protecting other metals, as in the tinware vessels in such common use, which are made of iron covered with a layer of tin. Copper vessels are also frequently covered with tin.

**Alloys.**—Bronze has already been treated of under Copper. It is made of copper, tin, and zinc. *Soft solder* is made of equal parts of tin and lead, or of two parts of tin and one of lead. *Britannia metal* is composed of nine parts of tin and one of antimony. *Tin amalgam* is made

by bringing tin and mercury together, and is used in the silvering of mirrors.

**Stannous Chloride, $SnCl_2$,** is formed by dissolving tin in hydrochloric acid, and if the solution is concentrated enough the compound crystallizes out. The crystals have the composition $SnCl_2 + 2H_2O$. This is the commercial product known as *tin salt*. It is very easily soluble in water, but if the solution is dilute it becomes turbid in consequence of the formation of the insoluble basic salt, $2Sn{<}{OH \atop Cl} + H_2O$:

$$2SnCl_2 + 3H_2O = 2Sn{<}{OH \atop Cl} + H_2O + 2HCl$$

This same decomposition takes place if the solution is allowed to stand in contact with the air. Under these circumstances a part of the stannous chloride is converted into stannic chloride by oxidation:

$$3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl.$$

When the crystals are heated they melt at about 40°, and if heated higher they undergo partial decomposition, forming the oxide and hydrochloric acid:

$$SnCl_2 + H_2O = SnO + 2HCl.$$

Stannous chloride has a marked tendency to combine with chlorine and to pass over into stannic chloride. This power has already been shown in its action upon mercuric chloride and upon mercurous chloride. It reduces the former, first to mercurous chloride, and it then abstracts the chlorine from this, leaving metallic mercury:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4 ;$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

Stannous chloride is an excellent mordant, and is extensively used by the dyers. It unites with other chlorides, forming double chlorides of the general formula $SnCl_2.2MCl$ or $M_2SnCl_4$, which are analogous to the salts of an unknown stannous acid, $H_2SnO_2$.

**Stannic Chloride, SnCl₄,** formed by treating tin with chlorine, is a colorless liquid which boils at 114°, and the specific gravity of its vapor is that required by a compound of the formula $SnCl_4$. In the air it gives off fumes in consequence of the action of moisture. It has long been known by the name *spiritus fumans Libavii,* which has reference to its fuming quality and to the fact that it was discovered by Libavius. It combines with water, forming a number of crystallized hydrates. When its solution in water is boiled stannic acid is precipitated :

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Probably the normal acid, $Sn(OH)_4$, is first formed, and this then breaks down with loss of water to form the ordinary acid :

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl ;$$
$$Sn(OH)_4 = SnO(OH)_2 + H_2O.$$

Stannic chloride is used as a mordant. With other chlorides it forms the *chlorostannates* of the general formula $M_2SnCl_6$ or $SnCl_4.2MCl$, of which the ammonium salt, $(NH_4)_2SnCl_6$, or *pink salt*, is the best known. This is manufactured for use in making cotton-prints. Similar fluorine compounds, the *fluostannates*, are also easily obtained, as $K_2SnF_6$, $Na_2SnF_6$, etc.

**Stannous Hydroxide, Sn(OH)₂,** is not known. When a solution of stannous chloride is treated with potassium carbonate a precipitate of the composition $H_2Sn_2O_3$ is formed, which is a derivative of the hydroxide $Sn(OH)_2$, as is shown by the formula $HO–Sn–O–Sn–OH$, which probably expresses its constitution. It readily loses water and passes over into *stannous oxide*, SnO, which is a black powder.

**Stannic Hydroxide, Sn(OH)₄,** is perhaps formed when a solution of stannic chloride in water is boiled. The precipitate obtained has, however, the composition $H_2SnO_3$, and this is known as *stannic acid.* Stannic acid is precipitated also by treating a solution of a stannate with

just enough of an acid to effect decomposition.   The decomposition with hydrochloric acid takes place as represented in the equation

$$Na_2SnO_3 + 2HCl = 2NaCl + H_2SnO_3.$$

The compound thus obtained is insoluble in water, but is easily soluble in hydrochloric, nitric, and sulphuric acids, and in the caustic alkalies.   With the alkalies it forms stannates, as *sodium stannate*, $Na_2SnO_3$, and *potassium stannate*, $K_2SnO_3$.   The former is made on the large scale, and is known as *preparing salt*.

*Metastannic Acid.*—When tin is treated with concentrated nitric acid it is converted into a white powder which is insoluble in water and in acids, but nevertheless seems to be a hydroxide of tin of the same composition as stannic acid.   This is known as *metastannic acid*.   With alkalies it forms salts which in properties and composition are entirely different from the stannates.   They are known as the *metastannates*.   Two sodium salts are known, which differ in composition.   One of these has the composition $Na_2Sn_5O_{11}$, the other is $Na_2Sn_9O_{19}$.   They are probably derived from acids analogous to the polysilicic acids, which may be called *polystannic acids*.   The question as to the composition of metastannic acid is an open one. When heated it is converted into the oxide $SnO_2$.   When treated with concentrated hydrochloric acid it is converted into a compound containing chlorine which is soluble in water, and the solution contains stannic chloride.   When this solution is treated with sulphuric acid stannic sulphate is thrown down, and when the solution is boiled this salt is decomposed, leaving stannic acid.

**Stannous Oxide, SnO,** is formed from the corresponding hydroxide when this is heated in a current of carbon dioxide.   When a solution of stannous chloride is treated with caustic soda stannous hydroxide is first precipitated, and this dissolves in an excess of the caustic soda.   When the solution is boiled the salt contained in it is decomposed, and black stannous oxide is thrown down in crystalline form.   When heated in the air stannous oxide takes fire, and is converted into stannic oxide.

**Stannic Oxide, $SnO_2$,** as has been stated, is the principal form in which tin occurs in nature. The mineral is known as cassiterite or tin-stone. It is found at Cornwall, England ; on the East Indian islands Banca and Biliton ; and in Malacca. It crystallizes in the tetragonal system, and is generally colored from brown to black. It is formed as a white powder by burning tin in the air, and by heating the different varieties of stannic hydroxide. It is infusible, and is not acted upon by concentrated hydrochloric or nitric acid. Concentrated sulphuric acid, however, converts it into a gelatinous liquid from which stannic oxide is precipitated by water.

**Stannous Sulphide, $SnS$,** which is formed when hydrogen sulphide is passed into a solution of stannous chloride, is a brownish-black powder. When treated with the soluble sulphides and sulphur, or with a soluble polysulphide, it dissolves, forming a sulphostannate as represented in these equations :

$$SnS + (NH_4)_2S + S = (NH_4)_2SnS_3 ;$$
$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

**Stannic Sulphide, $SnS_2$.**—This compound is obtained in crystallized form by heating together tin-filings, sulphur, and dry ammonium chloride ; and in amorphous form by treating a solution of stannic chloride with hydrogen sulphide. In the former case it is a golden-yellow crystalline substance ; in the latter a yellow powder. The crystalline variety is known as *mosaic gold*. When heated to a high temperature it is converted into stannous sulphide. The precipitated variety is easily dissolved by concentrated hydrochloric acid, and converted into metastannic acid by concentrated nitric acid. The crystallized variety is not soluble in hydrochloric acid, and is affected but slightly by nitric acid. The crystallized variety, or mosaic gold, is used as a pigment, particularly for bronzing. Stannic sulphide dissolves easily in the soluble sulphides, forming *sulphostannates :*

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3 ;$$
$$SnS_2 + K_2S = K_2SnS_3.$$

The sulphostannates are perfectly analogous in composition to the stannates, differing from them simply by containing three atoms of sulphur in place of the three atoms of oxygen. Although the comparison has been repeatedly made before in this book, it is perhaps not superfluous again to call attention to the analogy between the stannates, sulphostannates, chlorostannates, and fluostannates, all of which are easily obtained, and are well-characterized compounds. The formulas of some representatives of the four classes are here placed side by side :

$$K_2SnO_3 \qquad K_2SnS_3 \qquad K_2SnCl_6 \qquad K_2SnF_6$$
$$Na_2SnO_3 \qquad Na_2SnS_3 \qquad Na_2SnCl_6 \qquad Na_2SnF_6$$

When a solution of a sulphostannate is treated with an acid a yellow precipitate is formed. This becomes darker, and if filtered off and dried it forms a gray mass. It is thought that this may be sulphostannic acid, $H_2SnS_3$. It breaks down readily into hydrogen sulphide and stannic sulphide.

**Stannous and Stannic Salts.**—With acids, tin forms a few salts, but they are not particularly well characterized, and the stannic salts are easily decomposed by water. *Stannous sulphate*, $SnSO_4$, is formed by dissolving tin in warm concentrated sulphuric acid. *Stannic sulphate*, $Sn(SO_4)_2$, is precipitated when sulphuric acid is added to a dilute solution of stannic chloride. It is decomposed by hot water, forming stannic acid.

**Reactions which are of Special Value in Chemical Analysis.**—The reactions with hydrogen sulphide, and the conduct of the precipitated sulphides when treated with ammonium sulphide or polysulphide, are constantly utilized for analytical purposes when tin is present.

The reducing action of stannous compounds serves to distinguish them from stannic compounds.

The conduct of solutions of stannous and stannic compounds towards caustic alkalies has been explained above.

The *carbonates of the alkali metals* precipitate the hydroxides, and these do not dissolve in an excess of the carbonate. Metallic *zinc* precipitates the tin from a so-

lution of a tin compound as a spongy mass. If the precipitation is carried on in a platinum vessel the platinum is not colored by it. By this means tin can be distinguished from antimony, which is reduced under the same circumstances, but is deposited as a black coating upon the platinum.

### Lead, Pb (At. Wt. 205.36).

**General.**—The basic properties of lead are stronger, and its acidic properties weaker, than those of tin. Its principal compounds are those in which it acts as a base-forming element. The compounds in which it is quadrivalent, such as $PbO_2$, are comparatively unstable, and when treated with acids they readily pass over into the compounds of the series in which the lead is bivalent. Thus lead oxide itself readily gives up oxygen when treated with acids, and yields salts of bivalent lead.

**Forms in which Lead occurs in Nature.**—Lead occurs in nature as the sulphide, PbS, which is known as galenite or galena. Other natural compounds of the metal are the carbonate, $PbCO_3$, known as cerussite; the phosphate, $Pb_3(PO_4)_2$; the chromate, $PbCrO_4$, or crocoisite; and the molybdate, $PbMoO_4$, or wulfenite.

**Metallurgy.**—Most of the lead in the market is obtained from the sulphide, and as most of the sulphide contains silver both metals have to be considered in the treatment of the ore. Under the head of Silver (which see) reference was made to the methods by which this metal was separated from the lead after both have been separated from their compounds. Here it will only be necessary to show how the metals are extracted together from the ore. This is accomplished in one of two ways:

(1) By heating the sulphide with iron, when the latter combines with the sulphur, forming iron sulphide, while the lead is set free.

(2) By roasting the sulphide until it is partly converted into lead oxide and lead sulphate, and then heating the mixture without access of air, when two reactions take place, which are represented in these equations:

$$PbS + 2PbO = 3Pb + SO_2;$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

The lead is thus set free, and the sulphur is driven off as sulphur dioxide.

**Properties.**—Lead is a bluish-gray metal, with a high lustre. It is very soft, and not very strong; melts at 325°, and has the specific gravity 11.37. At a high temperature it is converted into vapor. When heated in contact with the air it becomes covered with a layer of oxide, as can be seen in a vessel containing the molten metal. In the air, at ordinary temperatures, it is tarnished in consequence of the formation of a suboxide of the composition $Pb_2O$. The formation of this compound can be observed very readily by cutting a piece of lead with a knife. At first the freshly-cut surface has a high lustre, but this soon grows dim and acquires a bluish color. Pure water acts upon lead when air has access to it, and some of the lead dissolves. If the water contains salts in solution, such as calcium carbonate, gypsum, etc., or if it contains carbon dioxide, it acts only very slightly upon the metal; further, water which contains organic matter in a state of decomposition dissolves lead with comparative ease. Nitric acid dissolves lead readily; as, however, lead nitrate is insoluble in nitric acid, it is necessary to use comparatively dilute acid. Concentrated sulphuric acid dissolves lead to some extent, and therefore a little lead sulphate is sometimes contained in commercial sulphuric acid. When such a solution is diluted with water the sulphate is precipitated. Hence, whenever the commercial acid is diluted with water it becomes turbid, and after standing for a time it becomes clear, as the lead sulphate settles. Hydrochloric acid acts only slightly upon lead. Acetic acid dissolves the metal very readily. It is precipitated in metallic form from a solution of one of its salts by metallic zinc. The formation is sometimes very beautiful, especially if the zinc is suspended in the solution. It is called the "lead tree," or *Arbor Saturni*. The action consists in a replacement of the lead by the zinc. After the action is complete all the lead is deposited as metallic lead, and the zinc has entered into its place,

forming a salt which remains in solution. Thus, if lead nitrate is used, zinc nitrate is in the solution.

**Applications.**—Lead is extensively used for a variety of purposes, as, for example, for making sulphuric-acid chambers, for evaporating-pans for alum and sulphuric acid, for shot, for water-pipes, and in making alloys. The use of lead water-pipes is a matter of much importance from the sanitary point of view, as is evident from the statements above made concerning the action of water upon the metal. Ordinary drinking-water acts under most circumstances only very slightly upon lead, and not enough is dissolved to be dangerous to those using the water. At the same time circumstances may at any time arise which will increase the solvent power of the water, and thus cause serious results; and it would undoubtedly be better if the use of such pipes could be entirely avoided in cases in which the water is to be used for drinking purposes.

**Lead Chloride, $PbCl_2$,** is formed when hydrochloric acid or a soluble chloride is added to a cold solution of a lead salt, and appears as a white precipitate. It is soluble in hot water, and is deposited in the form of long, needle-shaped crystals when the solution cools. It occurs in nature in small quantity, as cotunnite.

**Lead Tetrachloride, $PbCl_4$,** is a liquid that forms a crystalline mass at $-15°$. It is decomposed into the dichloride and chlorine at the ordinary temperature. At $105°$ this takes place with explosion. It is formed by passing chlorine into concentrated hydrochloric acid containing lead chloride. After saturation, ammonium chloride is added, when the double salt, $PbCl_4 . 2NH_4Cl$, separates in yellow crystals. Ice-cold concentrated sulphuric acid decomposes it into ammonium sulphate, hydrochloric acid, and lead tetrachloride, which collects as a yellow oil below the sulphuric acid.

**Lead Iodide, $PbI_2$,** is a yellow substance which crystallizes from water in beautiful lustrous laminæ. It is precipitated when potassium iodide is added to a solution of a lead salt. It dissolves in potassium iodide and forms a salt of the formula $PbI_2 . KI$ or $KPbI_3$. There

is also a hydrogen compound of the formula $H_2PbI_4$, that is formed by dissolving lead iodide in hydriodic acid.

**Lead Hydroxide, Pb(OH)₂**, is not known, but when a lead salt is treated with a soluble hydroxide a compound closely related to this hydroxide is formed. This varies somewhat in composition, according to the method by which it is made; but it is usually either HO–Pb–O–Pb–OH or HO–Pb–O–Pb–O–Pb–OH.

**Oxides of Lead.**—Lead forms four distinct compounds with oxygen, the formulas and names of which are as follows : *lead suboxide*, $Pb_2O$ ; *lead oxide*, PbO ; *lead sesquioxide*, $Pb_2O_3$ ; and *lead peroxide*, $PbO_2$.

**Lead Suboxide, Pb₂O.**—This compound, as has been stated, is formed when lead is exposed to the air. It has been made in pure condition, and is a black powder. When treated with acids it yields salts, and lead separates. Thus with hydrochloric acid lead chloride is formed, as represented in the equation

$$Pb_2O + 2HCl = PbCl_2 + H_2O + Pb.$$

**Lead Oxide, PbO.**—This compound is formed by heating lead nitrate, and is then left behind in the form of a yellow powder. If heated to melting it solidifies, forming a yellowish or reddish mass known as *litharge*. This is formed in large quantity in the process of separating silver from lead. It will be remembered that, in order to remove the last portions of lead from silver, the alloy is melted and air blown upon it in this condition. Under these circumstances, the lead is converted into the oxide while the silver remains unchanged. The lead oxide thus formed is the litharge found in the market. The oxide can be obtained in crystallized form by heating a solution of the ordinary oxide in dilute caustic soda or caustic potash ; and by boiling lead hydroxide with a quantity of caustic alkali insufficient to dissolve it. In the powdered condition lead oxide attracts carbon dioxide from the air. With acids it forms salts which in some respects resemble those of barium and strontium. With the strongest bases it forms salts similar to those

formed by zinc. This is seen in the solubility of the hydroxide in sodium and potassium hydroxide, which is due to the formation of compounds known as plumbites :

$$Pb(OH)_2 + 2KOH = Pb(OK)_2 + 2H_2O.$$

Heated with silicon dioxide it forms a silicate which is easily fusible. Lead oxide is used extensively in the manufacture of flint glass for optical purposes, as was described under Glass (which see). It also finds application in glass painting and porcelain painting, and is used in the manufacture of lead salts, particularly "sugar of lead," which is an acetate.

**Lead Sesquioxide, $Pb_2O_3$,** is obtained by bringing together lead acetate and caustic soda, and treating the solution with sodium hypochlorite ; and is thrown down as a reddish-yellow powder. The constitution of the compound is unknown. It has been suggested that it may be a lead salt of plumbic acid, as represented in the formula $PbO{<}^O_O{>}Pb$, plumbic acid being, as will be seen, $PbO{<}^{OH}_{OH}.$

**Lead Peroxide, $PbO_2$,** is formed by treating *minium* or *red lead* with dilute nitric acid. Minium has the composition, $Pb_3O_4$. When treated with nitric acid, a part dissolves as lead nitrate, and lead peroxide remains behind, as represented in the equation :

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

The peroxide is formed in general by the action of oxidizing agents upon the lower oxides of lead. One of the most convenient methods for making it consists in treating lead acetate with a filtered solution of bleaching-powder. It is a dark-brown powder, insoluble in water. When ignited it loses half of its oxygen, and it gives up its oxygen readily to other substances. Towards hydrochloric acid it acts like manganese dioxide, giving lead chloride and chlorine according to the equation

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

It appears probable that the tetrachloride is first formed, and that this then breaks down into the dichloride and chlorine. When the peroxide is treated in the cold with hydrochloric acid it dissolves, and when this solution is heated it gives off chlorine. Further, when it is treated with caustic alkalies lead peroxide is thrown down.

Lead peroxide dissolves in concentrated caustic potash and forms a salt of the formula $K_2PbO_3$, or $PbO{<}^{OK}_{OK}$, analogous to potassium stannate, $K_2SnO_3$, silicate, $K_2SiO_3$, carbonate, $K_2CO_3$, etc. Other salts derived from the acid $PbO(OH)_2$ are known, and are called *plumbates.*

*Red Lead, Minium.*—When lead oxide is heated gently in the air it takes up oxygen, and is converted into the red compound known as minium or red lead. The commercial article of this name varies in composition, but approximates to that represented by the formula $Pb_3O_4$, and, if the oxide is slowly heated, the amount of oxygen taken up is that required to form a compound of the above formula. Red lead varies in color from red to yellowish, according to the method of preparation. When heated, it becomes dark, but the red color appears again on cooling. When heated to a high temperature, it loses oxygen and yields lead oxide :

$$Pb_3O_4 = 3PbO + O.$$

When treated with dilute nitric acid, lead nitrate is formed, and lead peroxide is left undissolved. As regards the relation existing between minium and the other oxides of lead, no positive statement can be made. The evidence points to the conclusion that it is a chemical compound and not a mixture. Dilute acetic acid does not dissolve it, while this acid does dissolve the monoxide. It has been suggested that it is a lead salt of normal plumbic acid, $Pb(OH)_4$, as represented in the

formula $Pb\left\{\begin{array}{l} O \\ O \end{array}{>}Pb \\ \begin{array}{l} O \\ O \end{array}{>}Pb\right.$ . As partial experimental evidence

in support of this view, the fact may be mentioned that a compound similar to red lead is formed, when a solution of potassium plumbate is treated with a solution of lead oxide in potassium hydroxide. In solution, the potassium salt probably has the constitution repre-

sented by the formula $Pb\begin{cases} OH \\ OH \\ OK \\ OK \end{cases}$. When this is treated

with lead oxide the corresponding lead salt should be formed.—Red lead is used as a pigment, and sometimes in place of litharge when an oxide of lead is needed: as in the manufacture of glass, as a flux in the manufacture of porcelain, etc.

**Lead Sulphide, PbS.**—This has already been referred to as the principal compound from which lead is obtained. The natural variety is called galena or galenite. It is formed in the laboratory as a black precipitate, when hydrogen sulphide is passed into a solution of a lead salt. When heated in the air, as in the roasting of galenite, the sulphur passes off as sulphur dioxide, and the lead is converted into oxide. Concentrated hydrochloric acid dissolves it. Concentrated nitric acid converts it into the sulphate. When hydrogen sulphide is conducted into a weak acid solution of lead chloride, a compound containing lead, sulphur, and chlorine is precipitated, the composition of which is approximately that represented by the formula $3PbS.PbCl_2$, and this has a red or a yellow color, according to the conditions.

**Lead Nitrate, Pb(NO₃)₂.**—The nitrate is easily made by dissolving lead, lead oxide, or carbonate in nitric acid. The salt crystallizes well, and is easily soluble in water. It is difficultly soluble in dilute nitric acid, and insoluble in concentrated nitric acid, resembling in this respect barium nitrate. It is decomposed by heat, giving nitrogen peroxide, $NO_2$, and lead oxide.

**Lead Carbonate, PbCO₃.**—The carbonate occurs in nature as cerussite, crystallized in forms which are the same as those of barium carbonate, and of that variety of calcium carbonate known as aragonite. It can be ob-

tained by adding lead nitrate to a solution of ammonium carbonate, but, when solutions of lead salts are treated with the secondary carbonates of the alkali metals, precipitates of basic carbonates are always obtained. When an excess of sodium carbonate is added to a solution of lead nitrate, the precipitate has the composition HO–Pb–O–CO–O–Pb–O–CO–O–Pb–OH, or $3PbO.2CO_2 + H_2O$. The salts usually obtained are more complicated than this, but the relations between them and lead oxide and carbonic acid are of the same kind. Basic lead carbonate is prepared and used extensively, under the name of *white lead*, as a pigment. It is manufactured by different methods. The principal ones are the following:

(1) *The Dutch Method.*—This consists in exposing sheets of lead wound in spirals to the action of vinegar, air, and carbon dioxide from decaying organic matter. The spirals of sheet lead are placed in earthenware vessels, on the bottom of which, but not in contact with the lead, the vinegar is placed. The vessels thus arranged are placed in beds of horse manure. In consequence of decomposition, which is set up in the manure, carbon dioxide is given off slowly, and enough heat is generated to start the action upon the lead. The chemical changes involved in the process are, mainly, the formation of a basic acetate of lead, and the subsequent decomposition of this by carbon dioxide, forming a basic carbonate, and leaving the acetic acid free to act upon a further quantity of lead.

(2) *The French Method.*—In this method a solution of basic lead acetate is prepared by treating a solution of the neutral salt with lead oxide. This is then decomposed by passing carbon dioxide into it, when a basic carbonate is thrown down. The carbon dioxide is generally made by burning coke.

(3) *The English Method.*—This is a modification of the Dutch method, and differs from it chiefly in the replacement of manure by spent tan in a state of fermentation, and the use of dilute acetic acid in place of vinegar. There is less risk of discoloration in consequence of the formation of sulphuretted hydrogen, but the fermen-

tation takes place more slowly, and the whole process, therefore, requires a longer time.

The composition of white lead is not always the same. That prepared by precipitating a solution of basic lead acetate with carbon dioxide has the composition $Pb(OH)_2.3PbCO_3$; and that prepared by the Dutch method has the composition $Pb(OH)_2.2PbCO_3$; or these may be expressed structurally by the formulas

$$Pb{<}{OH \atop CO_3} \quad Pb{<}{OH \atop CO_3}$$
$$Pb{<}{CO_3 \atop CO_3} \quad Pb{<}{CO_3 \atop OH}$$
$$Pb{<}{CO_3 \atop OH} \quad and \quad Pb{<}{CO_3 \atop OH}.$$
$$Pb{<}{CO_3 \atop OH}$$

An objection to white-lead paint is that it turns dark under the influence of hydrogen sulphide. It also turns yellow in consequence of the action of some substance contained in the oil with which the lead carbonate is mixed.

**Lead Sulphate, $PbSO_4$,** occurs to some extent in nature. It is formed by adding sulphuric acid or a soluble sulphate to a solution of a lead salt, and by oxidation of lead sulphide. Like barium sulphate, it is practically insoluble in water. As stated above, it is somewhat soluble in concentrated sulphuric acid, and it is therefore always found in the concentrated acid of commerce. Nitric acid and hydrochloric acid dissolve it in considerable quantity. It dissolves further quite readily in solutions of some ammonium salts, as in ammonium tartrate and acetate. When heated to redness it is partly decomposed with loss of sulphur trioxide.

**Reactions which are of Special Value in Chemical Analysis.**—The reactions of lead salts with the soluble hydroxides, with sulphuric acid, hydrochloric acid, hydrogen sulphide, soluble carbonates, potassium chromate and dichromate, are the ones which are principally used in analysis. All of these have been treated of in this chapter, with the exception of those with potassium chromate and dichromate, which will be taken up in the chapter on Chromium (which see). In anticipation it

may be said that the reactions are based upon the fact that lead chromate, $PbCrO_4$, like barium chromate, is insoluble in water.

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The elements of Family V, Group A, are vanadium, columbium, didymium, and tantalum. As they are closely related to the members of Group B, of the same family, they were treated of at the end of Chapter XVIII. in connection with the members of the phosphorus group. Among them the one which is least known is didymium. This in turn is more or less closely related to two other elements of nearly the same atomic weight which occur in Families III and IV. These are lanthanum and cerium. A few words in regard to these three rare elements will suffice for the present purpose.

### Lanthanum, Cerium, Didymium.

These three elements occur together in several rare minerals of Norway, as cerite, gadolinite, and allanite. Cerite is a silicate of the three metals, and its composition is represented by the formula $\left.\begin{array}{c} Ce_4 \\ La_4 \\ Di_4 \end{array}\right\}(SiO_4)_3 + 3H_2O.$ It is probably a mixture of three isomorphous silicates. The principal constituent is cerium silicate, $Ce_4(SiO_4)_3$. The perfect separation of the constituents of the mineral is a very difficult operation.

**Lanthanum, La** (**At. Wt. 137.59**), forms an oxide of the formula $La_2O_3$, analogous to that of aluminium. Its chloride also is analogous to that of aluminium, and has the composition $LaCl_3$; and in all its salts it acts as a trivalent element.

**Cerium, Ce** (**At. Wt. 139.1**), forms two series of compounds, in one of which it is trivalent, resembling lanthanum and the other members of the aluminium group; while in the other series it is quadrivalent, resembling silicon and the other members of the silicon group. The formulas of some of the principal members of the first series are as follows:

$$CeCl_3, \ Ce_2O_3, \ and \ Ce_2(SO_4)_3.$$

Some of the principal members of the second series are represented by the formulas

$$CeF_4, \ CeO_2, \ Ce(NO_3)_4, \ \text{and} \ Ce(SO_4)_2.$$

**Didymium, Di** (**At. Wt. 142.1**), has already been referred to on page 351 in connection with the members of Family V, Group A, which it resembles in some respects. In most of its compounds it is, however, trivalent, forming compounds, of some of which the following are the formulas :

$$DiCl_3, \ Di_2O_3, \ Di(NO_3)_3, \ Di_2(SO_4)_3, \ Di_2(CO_3)_3, \ \text{etc.}$$

**Praseodymium, Pr, and Neodymium, Nd.**—While the name didymium is still given above, and this substance dealt with as though it were an element, as it was at first held to be, it has been shown by Auer von Welsbach that it consists of two very similar elements to which he has given the names *praseodymium* and *neodymium*. When the double nitrate of ammonium and didymium is repeatedly recrystallized it is separated into two salts, one of which is green, and the other rose-colored. When the nitrate or oxalate of one of these new elements is ignited it forms a black oxide, while from the other is formed an oxide of a different color. The element that gives green salts is called praseodymium, and the other neodymium. The atomic weights of these elements are nearly the same, but they have not yet been accurately determined.

# CHAPTER XXXI.

**General.**—At the end of Chapter XIV., in connection with the elements of the sulphur group, the four elements which form the subject of this chapter were briefly referred to, for the reason that in some respects they resemble sulphur. As was there stated, this resemblance "is seen mainly in the formation of acids of the formulas $H_2CrO_4$, $H_2MoO_4$, $H_2WO_4$, and $H_2UO_4$; and the oxides $CrO_3$, $MoO_3$, $WO_3$, and $UO_3$." Further, it was stated that "when the acids of chromium, molybdenum, tungsten, and uranium lose oxygen, they form compounds which have little or no acid character. The lower oxides of chromium form salts with acids, and these bear a general resemblance to the salts of aluminium, iron, and manganese. The chromates lose their oxygen quite readily when acids are present with which the chromium can enter into combination as a base-forming element." "Molybdenum and tungsten do not form salts of this character: indeed they seem to be practically devoid of the power to form bases. Uranium, on the other hand, forms some curious salts which differ from the simple metallic salts which we commonly have to deal with. These are the *uranyl* salts which are regarded as acids, in which the hydrogen is either wholly or partly replaced by the complex $UO_2$, which is bivalent. Thus, the nitrate has the formula $UO_2(NO_3)_2$, the sulphate $(UO_2)SO_4$, etc. These salts are derived from the compound $UO_2(OH)_2$, acting as a base, whereas the compound has also distinctly acid properties." That member of the group the compounds of which are most commonly met with in the laboratory and in the arts is chromium, and this will receive principal attention here.

## CHROMIUM, Cr (At. Wt. 51.74).

**General.**—This element forms three series of compounds, in which it appears to be respectively bivalent, trivalent, and sexivalent. Of these the members of the series in which it is trivalent are most stable under ordinary circumstances. Some of the principal members of the first series, or the *chromous compounds,* are represented by the formulas

$$CrCl_2, \ Cr(OH)_2, \ CrSO_4, \ CrCO_3.$$

Of the second series, or the *chromic compounds,* some of the principal members are :

$$CrCl_3, \ Cr_2O_3, \ Cr_2(SO_4)_3, \ Cr(NO_3)_3, \ KCr(SO_4)_2 + 12H_2O.$$

And, finally, the members of the third series are derived from the oxide $CrO_3$, and they are for the most part salts of the acid of the formula $H_2CrO_4$, known as *chromic acid,* or of an acid of the formula $H_2Cr_2O_7$, known as *dichromic acid,* which is closely related to chromic acid.

When exposed to the air the chromous compounds are converted into chromic compounds, and they are in general readily converted into chromic compounds by the action of oxidizing agents, as cuprous and mercurous compounds are converted into cupric and mercuric compounds. If the oxidation takes place in acid solution the limit is reached when a chromic salt is formed. If, however, the action takes place in the presence of a strong base the limit is reached in the formation of a chromate. Thus, suppose chromous oxide to be treated with an oxidizing agent in the presence of sulphuric acid, the final product would be chromic sulphate, as represented in the following equations :

$$CrO + H_2SO_4 = CrSO_4 + H_2O \ ;$$
$$2CrSO_4 + H_2SO_4 + O = Cr_2(SO_4)_3 + H_2O.$$

On the other hand, if the oxidation takes place in the presence of caustic potash the final product is potassium chromate, as shown in the following equation :

$$CrO + 2KOH + O_2 = K_2CrO_4 + H_2O.$$

When a chromate is treated with an acid it tends to pass back to a compound of the chromic series, and the change involves the giving up of oxygen. Thus when potassium chromate is treated with sulphuric acid in the presence of something which has the power to take up oxygen, potassium and chromium sulphates are formed, and oxygen is given up, thus:

$$2K_2CrO_4 + 5H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 3O.$$

All these relations will be more fully taken up in the paragraphs which treat of the individual compounds.

**Forms in which Chromium Occurs in Nature.**—The principal form in which chromium occurs in nature is the mineral chromite, also known as chromic iron and chrome iron ore. This has the composition $FeCr_2O_4$, and, as will be pointed out below, it is probably analogous to the spinels (see p. 572), being an iron salt of the acid $CrO.OH$, which may be called metachromous acid. This view is represented by the formula $\begin{array}{c}CrO.O\\CrO.O\end{array}>Fe$. It occurs also in the mineral crocoisite, which is lead chromate, $PbCrO_4$. The name chromium is derived from the Greek $\chi\rho\tilde{\omega}\mu\alpha$, meaning color; and the element is so called because most of its compounds are colored.

**Preparation.**—The metal is obtained by the electrolysis of chromic chloride; by decomposing the chloride by means of sodium in the form of vapor; and by treating the chloride with zinc.

**Properties.**—Chromium is a light-gray, crystalline, lustrous, metallic-looking substance; or it consists of microscopic, lustrous rhombohedrons of a tin-white color. It is very hard, and difficultly fusible. When heated in the air it is oxidized very slowly, but in the flame of the oxyhydrogen blowpipe it burns, forming chromic oxide, $Cr_2O_3$. It is easily dissolved by hydrochloric acid. Cold sulphuric acid does not dissolve it; the hot acid does. Nitric acid does not affect it. When treated with salts of potassium which easily give up their oxygen, as the chlorate and nitrate, it is converted into potassium chromate.

**Chromous Chloride, CrCl₂,** is formed by dissolving the metal in hydrochloric acid, and by carefully heating chromic chloride in a current of hydrogen. It forms white crystals, which dissolve in water, giving a blue solution. This solution takes up oxygen very readily from the air, and the compound is converted into others which belong to the chromic series. The other chromous compounds act in a similar way.

**Chromic Chloride, CrCl₃.**—This compound is made in solution by dissolving chromic hydroxide, $Cr(OH)_3$, in hydrochloric acid. This solution has a dark-green color. When evaporated to a sufficient extent crystals of the composition $CrCl_3 + 6H_2O$ are deposited. If these are heated in the air they undergo decomposition just as aluminium chloride does, and the product left behind is chromic oxide :

$$2CrCl_3 + 3H_2O = Cr_2O_3 + 6HCl.$$

If, however, the crystallized chloride is heated in an atmosphere of chlorine or hydrochloric acid, the water is given off, and the anhydrous chloride, which has a beautiful reddish violet color, is formed. This dissolves in water and forms a green solution. But if the dry chloride thus obtained is sublimed, it is deposited in lustrous laminæ of the same color ; and this variety is insoluble in water and acids, and is only slowly acted upon by boiling alkalies. This insoluble, crystallized variety of the chloride is obtained also by the same method as that used in making aluminium chloride, that is, by passing a current of chlorine over a heated mixture of carbon and chromic oxide. Although it is called insoluble, it passes gradually into solution by boiling with water. Further, when a very minute quantity of chromous chloride is mixed with it, it dissolves easily, and forms a green colored solution.

Chromic chloride unites with other chlorides, as aluminium chloride does, and forms double chlorides, analogous to the chlor-aluminates. Examples of these are the compounds of the formulas $CrCl_3.KCl$, or

$KCrCl_4$; $CrCl_3.2KCl$, or $K_2CrCl_5$; and $CrCl_3.3KCl$, or $K_3CrCl_6$.

**Chromous Hydroxide, Cr(OH)₂,** is formed as a brownish-yellow precipitate by adding caustic potash to a solution of chromous chloride. It easily gives up hydrogen, and is converted into chromic oxide :

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

**Chromic Hydroxide, Cr(OH)₃.**—When ammonia is added to a solution of a chromic salt, a light-blue voluminous precipitate, which has the composition $Cr(OH)_3 + 2H_2O$, is formed. When this is filtered off and dried in a vacuum it loses the water and leaves the hydroxide. This is readily converted by heat into a compound of the formula $CrO.OH$, and finally into chromic oxide, $Cr_2O_3$. The green precipitates formed in solutions of chromic salts by sodium and potassium hydroxides always contain some of the alkali metal in combination.

Chromic hydroxide, like aluminium hydroxide, dissolves in the soluble hydroxides, and forms salts known as chromites, which are derived from the acid $CrO.OH$. Thus with potassium hydroxide the action takes place as represented in the equation

$$Cr{\Large\langle}^{OH}_{OH}_{OH} + KOH = Cr{\Large\langle}^{O}_{OK} + 2H_2O.$$

If the solution containing potassium or sodium chromite is boiled, the salt is decomposed and chromic hydroxide precipitated, though the precipitate thus formed always contains some of the alkali metal in combination. It will be noticed that in this respect aluminium and chromium conduct themselves differently towards the alkaline hydroxides.

It has already been stated that chromite, $(CrO.O)_2Fe$, is regarded as an iron salt of the same order as the potassium salt referred to.

Another hydroxide formed by heating potassium dichromate and boric acid together has the composition represented by the formula $Cr_2O(OH)_4$ or $Cr_4O_3(OH)_6$. This is known as *Guignet's green.* The relation between the normal hydroxide and these compounds is shown by means of the equations

$$2Cr(OH)_3 = Cr_2O(OH)_4 + H_2O\,;$$
$$4Cr(OH)_3 = Cr_4O_3(OH)_6 + 3H_2O.$$

**Chromic Oxide, $Cr_2O_3$,** is formed by igniting the hydroxides, and is most readily prepared by heating a mixture of potassium dichromate and sulphur. The sulphur is oxidized, and with the potassium forms potassium sulphate, while the chromic acid is reduced to the form of the oxide $Cr_2O_3$. It can be obtained in crystals. As ordinarily obtained it is a green powder, which after ignition is almost insoluble in acids. It is dissolved, however, by treatment with fusing potassium sulphate. The oxide colors glass green, and is used in painting porcelain.

**Chromic Sulphate, $Cr_2(SO_4)_3$,** is made by dissolving the hydroxide in concentrated sulphuric acid when it is deposited in purple crystals of the composition $Cr_2(SO_4)_3 + 15H_2O$. If the solution of this salt is boiled, the solution becomes green, and crystals cannot be obtained from it. But by standing for some time the green solution becomes reddish purple again, and yields the crystallized salt. Other salts of chromium act in the same way. They exist in two varieties, one of which crystallizes and is reddish purple in color, while the other does not crystallize and is green. The crystallized salts are converted into the uncrystallized green salts by boiling, and the green salts are converted into the crystallized salts by standing.

**Chrome-Alums.**—Chromic sulphate, like aluminium sulphate, combines with other sulphates, such as potassium, sodium, and ammonium sulphates, and forms well-crystallized salts, which are closely analogous to ordinary

alum. They all contain twelve molecules of water, as represented in the formulas below:

| | | |
|---|---|---|
| Chrome-Alum, . . . . . . | $KCr(SO_4)_2$ | $+ 12H_2O$ |
| Sodium Chrome-Alum, . . . | $NaCr(SO_4)_2$ | $+ 12H_2O$ |
| Ammonium Chrome-Alum, . | $(NH_4)Cr(SO_4)_2$ | $+ 12H_2O$ |

The potassium compound which is commonly called chrome-alum is made by adding a reducing agent, such as alcohol or sulphur dioxide, to a solution of potassium dichromate containing sulphuric acid. If the solution is heated it turns green, and crystals cannot be obtained from it. But on standing for a considerable time its color changes, and reddish-purple crystals of the alum are deposited. This change can be facilitated by putting some crystals of the salt in the concentrated green solution. The action of reducing agents upon potassium dichromate will be treated of farther on. The salt finds application in dyeing and tanning.

**Chromic Acid and the Chromates.**—It has already been stated that when chromium compounds belonging to the chromous and chromic series are oxidized in the presence of bases they are converted into chromates. These salts are derived from an acid of the formula $H_2CrO_4$, which is unknown, as it breaks down spontaneously into chromium trioxide, $CrO_3$, and water, when it is set free from its salts, just as carbonic and sulphurous acids break down respectively into carbon dioxide and water, and sulphur dioxide and water. The starting-point for the preparation of the chromates and the compounds related to them is chromic iron. This is ground fine, intimately mixed with a mixture of caustic potash and lime, and then heated in shallow furnaces in contact with the air. Under these circumstances oxidation is effected by the oxygen of the air. The iron is converted into ferric oxide, and the chromium gives, with the calcium and potassium, the corresponding chromates, $CaCrO_4$ and $K_2CrO_4$. When the mass is treated with water these salts dissolve, and ferric oxide remains undissolved. By treating the solution with potassium sulphate the calcium salt is converted into the potassium salt, and thus

all the chromium appears in the form of potassium chromate, the changes referred to are represented in the following equations :

$$2(CrO_2)_2Fe + 8KOH + 7O = 4K_2CrO_4 + Fe_2O_3 + 4H_2O ;$$
$$2(CrO_2)_2Fe + 4CaO + 7O = 4CaCrO_4 + Fe_2O_3 ;$$
$$CaCrO_4 + K_2SO_4 = K_2CrO_4 + CaSO_4.$$

As potassium chromate is easily soluble in water, and therefore difficult to purify, it is converted into the dichromate, which is less soluble and crystallizes well. The change is easily effected by adding the necessary quantity of a dilute acid. If nitric acid is used the reaction is represented by the following equation :

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

The salt thus obtained is manufactured on the large scale and is the starting-point for the preparation of other chromium compounds.

**Potassium Chromate, $K_2CrO_4$,** formed as above described, is a light-yellow crystallized substance which is easily soluble in water. It is isomorphous with potassium sulphate. Acids convert it into the dichromate, as just stated.

**Potassium Dichromate, $K_2Cr_2O_7$.**—This salt forms large red plates, which are triclinic. It is soluble in ten parts of water at the ordinary temperature, and is much more soluble in hot water. When heated, it at first melts without undergoing decomposition ; at white heat, however, it is decomposed, yielding the chromate, chromic oxide, and oxygen :

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + 3O.$$

It undergoes a similar change, but much more readily, when heated with concentrated sulphuric acid. In this case, however, the chromic oxide forms chromic sulphate with the acid, and this forms chrome-alum with the potassium sulphate :

$$K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O.$$

All the oxygen in the chromate in excess of that required

to form the alum and water is given off. This also is the character of the action towards reducing agents in general. One molecule of the dichromate gives three atoms of oxygen. With sulphur dioxide the action is that represented in the equation

$$K_2Cr_2O_7 + 4H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + 3H_2SO_4 + H_2O.$$

Or, one molecule of the dichromate converts three molecules of sulphur dioxide, $SO_2$, into three molecules of sulphuric acid, $H_2SO_4$.

The action with alcohol will be understood by the aid of the following equation, which represents the action of oxygen in general upon alcohol:

$$\underset{\text{Alcohol}}{C_2H_6O} + O = \underset{\text{Aldehyde}}{C_2H_4O} + H_2O.$$

Each molecule of alcohol requires one atom of oxygen to convert it into aldehyde. Therefore, one molecule of the dichromate oxidizes three molecules of alcohol to aldehyde:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O = 2KCr(SO_4)_2 + 3C_2H_4O + 7H_2O.$$

Concentrated hydrochloric acid is oxidized by the dichromate, and chlorine is evolved:

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 6Cl.$$

Here two atoms of chlorine are required to form potassium chloride with the potassium, and six to form chromic chloride with the chromium; and the eight hydrogen atoms in combination with this chlorine combine with four atoms of oxygen of the dichromate, leaving three more to oxidize hydrochloric acid. Consequently one molecule of the dichromate sets free six atoms of chlorine:

$$3O + 6HCl = 3H_2O + 6Cl.$$

When the dichromate in solution is treated with potassium hydroxide, its color changes to yellow, in consequence of the formation of the chromate, the action taking place as represented in this equation:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Potassium dichromate finds extensive use in the arts and in the laboratory as an oxidizing agent. With gelatine it forms a mixture which is sensitive to light, which turns it dark, and makes it insoluble. This fact is made the basis of a number of photographic processes. The dichromate is used, further, in dyeing.

**Chromium Trioxide, $CrO_3$,** crystallizes out on cooling when either the chromate or the dichromate is treated in concentrated solution with concentrated sulphuric acid. This is a beautiful red substance, which crystallizes in needles. When dissolved in water it forms a solution from which, by neutralization, the chromates can be obtained. When heated alone it gives off half its oxygen, and is converted into chromic oxide:

$$2CrO_3 = Cr_2O_3 + 3O;$$

and when heated with sulphuric acid it gives chromic sulphate and oxygen:

$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O.$$

It is an extremely active oxidizing agent, disintegrating most organic substances with which it is brought in contact.

**Relations between the Chromates and Dichromates.—** The fact that chromium trioxide with water gives chromic acid, which is a dibasic acid, whose salts in general resemble those of sulphuric acid, leads to the belief that the structure of chromic acid should be represented by a formula similar to that of sulphuric acid, thus:

$$\begin{array}{cc}
O & O \\
\| & \| \\
HO{-}S{-}OH & HO{-}Cr{-}OH \\
\| & \| \\
O & O \\
\text{or} & \text{or} \\
O_2S(OH)_2 & O_2Cr(OH)_2
\end{array}$$

Just as sulphuric acid by loss of water is converted into disulphuric acid or pyrosulphuric acid, so chromic acid is converted into dichromic acid, and in all probability the relation between the chromates and dichromates is

the same as that between the sulphates and disulphates, as represented by the equations

$$SO_2 {<}^{OH}_{OH} \atop SO_2 {<}^{OH}_{OH} = SO_2 {<}^{OH}_{O} \atop SO_2 {<}^{OH}_{OH} + H_2O \; ;$$

$$CrO_2 {<}^{OH}_{OH} \atop CrO_2 {<}^{OH}_{OH} = CrO_2 {<}^{OH}_{O} \atop CrO_2 {<}^{OH}_{OH} + H_2O.$$

But, as has been stated, neither chromic acid nor dichromic acid is known, as they break down into chromium trioxide and water when set free from their salts. The conversion of potassium chromate into the dichromate by treatment with an acid is represented as follows :

$$CrO_2 {<}^{OK}_{OK} \atop CrO_2 {<}^{OK}_{OK} + {HNO_3 \atop HNO_3} = CrO_2 {<}^{OK}_{OH} \atop CrO_2 {<}^{OH}_{OK} + 2KNO_3 \; ;$$

$$CrO_2 {<}^{OK}_{OH} \atop CrO_2 {<}^{OH}_{OK} = CrO_2 {<}^{OK}_{O} \atop CrO_2 {<}^{OK}_{OK} + H_2O.$$

**Sodium Chromate, $Na_2CrO_4$, and Sodium Dichromate, $Na_2Cr_2O_7$,** are made in the same way as the potassium compounds. They are both deliquescent as ordinarily made. It has, however, recently been shown that a sodium dichromate which is not deliquescent can be made ; and at present it is largely manufactured instead of the somewhat more expensive potassium salt.

**Barium Chromate, $BaCrO_4$,** like the sulphate, is insoluble in water, and is precipitated when a solution of a barium salt is brought together with a soluble chromate or dichromate. It is soluble in hydrochloric acid and nitric acid, but not in acetic acid. The strontium salt is somewhat soluble in water, and easily in hydrochloric, nitric, and acetic acids.

**Lead Chromate, PbCrO₄,** occurs in nature, and is formed as a beautiful yellow precipitate when a solution of a lead salt is treated with a solution of a chromate or dichromate. It is used as a pigment under the name *chrome yellow.* When heated to a high temperature it gives off some of its oxygen. In contact with oxidizable substances it gives off its oxygen very easily, and it is used in the laboratory in some cases instead of cupric oxide in the analysis of organic compounds (see p. 594). Treated with dilute potassium or sodium hydroxide in insufficient quantity to dissolve it, it turns red in consequence of the formation of a basic chromate which is known as *chrome red.* The action takes place as represented in the equation

$$CrO_2 <^O_O> Pb \atop CrO_2 <^O_O> Pb \; + \; 2KOH = CrO_2 <^{O-Pb-OH}_{O-Pb-OH} + K_2CrO_4.$$

This then loses water, and forms the salt $CrO_2 <^{O-Pb}_{O-Pb}> O$, which is chrome red.

Lead chromate dissolves completely in the caustic alkalies in consequence of the formation of chromates and plumbites.

*Silver chromate,* $Ag_2CrO_4$, is formed as a red precipitate when a chromate is treated with a silver salt.

*Potassium trichromate,* $K_2Cr_3O_{10}$, and *potassium tetrachromate,* $K_2Cr_4O_{13}$, are formed by treating the dichromate with nitric acid :

$$3K_2Cr_2O_7 + 2HNO_3 = 2K_2Cr_3O_{10} + 2KNO_3 + H_2O \; ;$$
$$2K_2Cr_2O_7 + 2HNO_3 = K_2Cr_4O_{13} + 2KNO_3 + H_2O.$$

The acids from which these salts are derived bear to ordinary chromic acid relations similar to those which the polysilicic acids bear to ordinary silicic acid.

**Chromium Oxychloride, Chromyl Chloride, CrO₂Cl₂,** is analogous to sulphuryl chloride, $SO_2Cl_2$, and is to be

regarded as derived from chromic acid by the replacement of the hydroxyls by chlorine:

$$CrO_2{<}{OH \atop OH}; \qquad CrO_2{<}{Cl \atop Cl}.$$

It is formed by treating a mixture of sodium chloride and potassium dichromate with sulphuric acid. Probably the sulphuric acid sets free hydrochloric acid and chromic acid simultaneously, and these then act upon each other as represented in the equation

$$CrO_2{<}{\overline{OH \quad H}|Cl \atop \underline{OH + H}|Cl} = CrO_2{<}{Cl \atop Cl} + 2H_2O.$$

It is a dark-red-colored liquid, which boils at 116° without decomposition. With water it gives chromic acid and hydrochloric acid, and with an alkaline hydroxide it gives the corresponding chromate:

$$CrO_2{<}{Cl \atop Cl} + {HHO \atop HHO} = CrO_2{<}{OH \atop OH} + 2HCl;$$

$$CrO_2{<}{Cl \atop Cl} + {KOH \atop KOH} = CrO_2{<}{OK \atop OK} + 2HCl.$$

**Reactions which are of Special Value in Chemical Analysis.**—The reactions of chromic salts with the *alkaline hydroxides* have been explained. With the *soluble carbonates* they give precipitates which consist mainly of the hydroxide, though carbonic acid is to some extent in combination in them. These precipitates are soluble in a large excess of the carbonate.

The solution of chromic oxide in an alkali is green, but by oxidizing agents it is turned yellow in consequence of the formation of a chromate.

*Hydrogen sulphide* does not precipitate chromium from its salts. *Ammonium sulphide* precipitates chromium hydroxide, the reaction being the same as in the case of aluminium (which see).

*Chromates* give with barium and lead salts yellow precipitates (see Barium Chromate and Lead Chromate).

When heated with sulphuric acid, the chromates are decomposed, with evolution of oxygen. The action of hydrochloric acid upon the chromates was explained above.

In neutral or slightly acid solutions of chromates, hydrogen sulphide and ammonium sulphide act as reducing agents, and precipitate the hydroxide mixed with sulphur:

$$K_2Cr_2O_7 + 3H_2S + 2HCl = 2KCl + 2Cr(OH)_3 + 3S + H_2O.$$

With borax or microcosmic salt chromium compounds form green beads, both in the oxidizing and reducing flames.

## MOLYBDENUM, Mo (At. Wt. 95.26).

**General.**—Molybdenum is of interest on account of the variety of its compounds. It forms four compounds with chlorine, the formulas of which appear to be $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. With oxygen also it forms four compounds, but, while the first three are analogous to the first three chlorine compounds above mentioned, the last differs from the last chlorine compound. In it the element is sexivalent. The formulas of the oxygen compounds are $MoO$, $Mo_2O_3$, $MoO_2$, and $MoO_3$. The last of these is analogous to chromium trioxide, as it forms salts with bases analogous to the chromates, and known as the molybdates.

**Occurrence and Preparation.**—Molybdenum occurs in nature principally as molybdenite, which is the sulphide $MoS_2$, and as wulfenite, which is lead molybdate, $PbMoO_4$. It occurs also, but in smaller quantity, as molybdenum trioxide, $MoO_3$. It is obtained in free condition by heating the oxides or chlorides in a current of hydrogen.

**Properties.**—It is a very hard silver-white metal of specific gravity 8.6. It is apparently infusible when pure. When heated for a considerable time in the air it is converted into the trioxide. It dissolves in concentrated nitric acid and in *aqua regia*.

**Chlorides.**—When molybdenum is heated for a long time in a current of chlorine it is finally completely converted into the pentachloride, $MoCl_5$. When the penta-

chloride is heated to 250° in a current of hydrogen it is converted into the trichloride, $MoCl_3$. And when the trichloride is heated in a current of carbon dioxide it is converted into the dichloride and the tetrachloride :

$$2MoCl_3 = MoCl_2 + MoCl_4.$$

**Oxides.**—The final product of the action of oxygen or oxidizing agents upon molybdenum is the trioxide, $MoO_3$. This is obtained comparatively easily when molybdenite, $MoS_2$, is mixed with pure sand and roasted, then treated with ammonia, which forms ammonium molybdate. This salt is crystallized, and afterwards decomposed by nitric acid. The oxide is a white crystallized substance which is difficultly soluble in water. When a solution of the trioxide is treated with reducing agents, as sodium-amalgam, lower oxides are formed, and the reduction stops at *molybdic oxide*, $Mo_2O_3$. This is a black compound. The *dioxide*, $MoO_2$, is a dark-blue substance which is formed by gently heating the metal or molybdic oxide, $Mo_2O_3$, in the air, and also by heating the corresponding hydroxide, $Mo(OH)_4$.

*Molybdenum monoxide*, MoO, is formed by treating a solution of the dichloride with hot caustic potash. Like molybdic oxide it is black.

*Molybdenum trisulphide*, $MoS_3$, is precipitated as a reddish-brown substance when a moderately concentrated solution of a molybdate is treated with hydrogen sulphide. When heated it is converted into the *disulphide*, $MoS_2$, which is identical in composition with the molybdenite found in nature.

**Molybdic Acid and the Molybdates.**—Molybdenum trioxide, $MoO_3$, combines readily with bases, forming salts which in composition are analogous to the chromates. When ammonium molybdate is treated with moderately dilute nitric acid free molybdic acid crystallizes out. This has the composition represented by the formula

$$H_2MoO_4 + H_2O, \text{ and perhaps the constitution } MoO \begin{cases} OH \\ OH \\ OH \\ OH \end{cases}$$

analogous to that of tetrahydroxyl-sulphuric acid. Molybdic acid not only forms compounds with bases, but also with acids. The latter are, however, not salts, but complex acids which in turn form salts with bases, some of which are extremely complicated. There are a number of molybdates known of the general formula $M_2MoO_4$, in which M represents a univalent element, but the acid further shows a marked tendency to form more complex salts, derivatives of polymolybdic acids. Thus the following sodium salts are known : $Na_2MoO_4$, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$, $Na_2Mo_4O_{13}$, $Na_2Mo_8O_{25}$, $Na_2Mo_{10}O_{31}$, and $Na_4Mo_7O_{24}$. The relations between the acids from which these salts are derived, and molybdic acid, $H_2MoO_4$, will readily be seen by the aid of the following equations :

$$2H_2MoO_4 = H_2Mo_2O_7 + H_2O ;$$
$$3H_2MoO_4 = H_2Mo_3O_{10} + 2H_2O ;$$
$$4H_2MoO_4 = H_2Mo_4O_{13} + 3H_2O ;$$
$$8H_2MoO_4 = H_2Mo_8O_{25} + 7H_2O ;$$
$$10H_2MoO_4 = H_2Mo_{10}O_{31} + 9H_2O ;$$
$$7H_2MoO_4 = H_8Mo_7O_{24} + 4H_2O.$$

**Lead Molybdate, $PbMoO_4$,** occurs in nature, as has been stated, and the mineral is known as wulfenite. It can be obtained artificially by melting together sodium molybdate, lead chloride, and sodium chloride ; or by treating a solution of sodium molybdate with a solution of lead nitrate. If the reagents are pure the artificially prepared salt is white, while the natural variety is always yellow or red.

**Phospho-molybdic Acid.**—Among the best known and most frequently met with compounds of molybdic acid with acids is that which it forms with phosphoric acid, known as *phospho-molybdic acid.* When a solution of ammonium molybdate in an excess of nitric acid is added in excess to a solution of phosphoric acid or a phosphate, a yellow precipitate is formed. This is *ammonium phospho-molybdate*, which, when dried, has the composition represented by the formula $12MoO_3.(NH_4)_3PO_4$. This is insoluble in water and in dilute acids, and also in a nitric-

acid solution of ammonium molybdate. On account of the properties mentioned, this salt furnishes a valuable means of detecting phosphoric acid and of precipitating it from its solutions. When the salt is treated with *aqua regia* it is decomposed, and from the solution formed a compound of the composition $H_3PO_4.11MoO_3 + 12H_2O$ crystallizes out.

## Tungsten, W (At. Wt. 183.43).

**General.**—Like molybdenum, tungsten forms a large variety of compounds. With chlorine it forms four, of which the formulas are $WCl_2$, $WCl_4$, $WCl_5$, and $WCl_6$. With oxygen, however, it forms but two compounds, and these are represented by the formulas $WO_2$ and $WO_3$. The trioxide forms salts with bases which are analogous to the molybdates, and, like molybdic acid, tungstic acid forms complicated salts which are derived from poly-tungstic acids. Further, tungstic acid combines with other acids, forming very complex acids.

**Occurrence and Preparation.**—Tungsten occurs in nature as tungstates. The principal one is the iron salt, which always, however, contains some manganese. This is known as wolframite, and has the composition represented by the formula $FeWO_4$. Calcium tungstate, $CaWO_4$, or scheelite, and lead tungstate, $PbWO_4$, or stolzite, are also found in nature, but in smaller quantity than wolframite. The element is prepared by reducing the chlorides or oxides in a current of hydrogen.

**Properties.**—Tungsten forms lustrous, steel-colored laminæ, or a black powder. It is very hard and difficultly fusible, and has the specific gravity 19.129. It is not changed by contact with the air at ordinary temperatures. At higher temperatures it combines with oxygen and forms the trioxide, $WO_3$. Nitric acid and *aqua regia* convert it into the trioxide. It is used in the manufacture of steel, as the addition of from 8 to 9 per cent of it makes steel extremely hard.

**Chlorides.**—When tungsten is heated in a current of chlorine it is converted into the hexachloride, $WCl_6$. The other chlorides are formed by heating this in hydrogen.

**Oxides.**—*Tungsten trioxide*, $WO_3$, is found in small quantity in nature, and is formed from wolframite by a number of methods. When a solution of a tungstate is boiled with an acid the trioxide is precipitated as a yellow powder. Under the influence of sunlight it turns greenish. It is insoluble in water. In alkalies it dissolves, forming the tungstates. When heated in a current of hydrogen, lower oxides are formed; and a blue compound thus obtained appears to have the composition represented by the formula $2WoO_3 + WO_2$ or $W_3O_8$. The *dioxide*, $WO_2$, is obtained by further reduction. This is a brown powder.

**Tungstic Acid and the Tungstates.**—When the required quantities of tungsten trioxide and potassium carbonate are brought together in solution, or are melted together, potassium tungstate, $K_2WO_4$, is formed. If a solution of this salt is treated with a strong acid at the ordinary temperature, a white precipitate of the composition $H_2WO_4 + H_2O$ is formed. This is tungstic acid, analogous to crystallized molybdic acid. If the solutions are hot the precipitate has the composition $H_2WO_4$. Among the complex salts derived from polytungstic acids are the following: $Na_2W_2O_7$, $Na_4W_3O_{11}$, $Na_{10}W_{12}O_{41}$, etc. The relations between the polytungstic acids and the ordinary variety of the acid, $H_2WO_4$, will be readily understood. The salt, $Na_{10}W_{12}O_{41} + 28H_2O$, is known as *sodium paratungstate*. It is manufactured on the large scale by heating together wolframite and calcined sodium carbonate. Inflammable substances impregnated with a solution of the salt burn with great difficulty, and it is used to protect various articles from fire. The salts derived from the acid, $H_2W_4O_{13}$, are called *metatungstates*.

**Silico-tungstic Acids.**—Among the most interesting of the complex compounds formed by the combination of tungstic acid with other acids are those known as the *silico-tungstic acids*. When sodium paratungstate, $Na_{10}W_{12}O_{41}$, is boiled in solution with precipitated gelatinous silicic acid, the latter dissolves, and from the solution a salt of the composition $Na_8W_{12}SiO_{42} + 7H_2O$ crystallizes. This is soluble in one fifth its weight of water,

and the solution has the remarkably high specific gravity 3.05. The acid from which the salt is derived is known as silico-tungstic acid. Its composition is represented by the formula $4H_2O.12WO_3.SiO_2$; and it may be regarded as made up of a polytungstic acid, $H_8W_{12}O_{40}$, in combination with one molecule of silicon dioxide, $H_8W_{12}O_{40}.SiO_2$.

## URANIUM, U (At. Wt. 237.77).

**General.**—Uranium has stronger basic properties than either molybdenum or tungsten; and it differs from chromium in the fact that the trioxide forms salts with acids. These salts are the uranyl salts which are derived from the hydroxide, $UO_2(OH)_2$ or $H_2UO_4$. The corresponding compounds of chromium, molybdenum, and tungsten are acids. Uranium also forms salts in which it acts as a quadrivalent element, as $U(SO_4)_2$. While the hydroxide, $UO_2(OH)_2$, forms salts with acids, it also forms salts with the strongest bases. These are analogous in composition to the dichromates, and have the general formula $M_2U_2O_7$. With chlorine, uranium forms the compounds $UCl_3$, $UCl_4$, and $UCl_5$; and with oxygen the following: $UO_2$, $U_3O_8$, $UO_3$, and $UO_4$.

**Occurrence and Preparation.**—Uranium occurs in nature chiefly in the form of the mineral known as pitchblende or uraninite, which consists of the oxide, $U_3O_8$, mixed with a number of other substances in smaller or larger quantities. When this is finely powdered and treated with concentrated nitric acid, uranyl nitrate, $UO_2(NO_3)_2$, is obtained, and, by igniting this, the trioxide, $UO_3$, is left behind. In order to isolate the metal, the oxide thus obtained is mixed with charcoal and treated with chlorine, when the tetrachloride, $UCl_4$, is formed. This is then reduced by heating it with sodium under a cover of the molten chlorides of potassium and sodium.

**Properties.**—Uranium has the color of nickel and the specific gravity 18.4. When heated to redness it is oxidized superficially. It dissolves in dilute acids with evolution of hydrogen.

**Chlorides.**—When chlorine acts upon finely divided uranium, the two combine to form the *tetrachloride*, $UCl_4$. When this is heated in hydrogen it loses a part of its chlorine and forms the *trichloride*, $UCl_3$; and when the tetrachloride is treated with chlorine it is partly converted into the *pentachloride*, $UCl_5$. The tetrachloride is the most stable form.

**Oxides.**—The oxide of uranium which is formed as the last product of the action of oxygen on uranium or the other oxides when these are heated in the air is that which has the composition $U_3O_8$, which is also the composition of the natural variety. When this is treated with nitric acid, however, it is converted into uranyl nitrate, $UO_2(NO_3)_2$, which is a derivative of the *trioxide*, $UO_3$; and when the nitrate is ignited, the trioxide is left behind. By reduction with hydrogen the trioxide is converted into the *dioxide*, $UO_2$; and when either the dioxide or the trioxide is heated in the air, the product obtained is the oxide $U_3O_8$. As will be pointed out below, this is regarded as a uranium salt of uranic acid.

**Uranous Salts.**—In the uranous salts, uranium acts as a quadrivalent element, replacing four atoms of hydrogen, as, for example, in the sulphate, which has the composition $U(SO_4)_2$. But few salts of this order are known.

**Uranyl Salts.**—As already explained, the uranyl salts are derivatives of the hydroxide $UO_2{<}^{OH}_{OH}$, and are formed by the action of acids, as represented in the equations below:

$$UO_2{<}^{OH}_{OH} + {}^{HO}_{HO}{>}SO_2 = UO_2{<}^{O}_{O}{>}SO_2 + 2H_2O;$$

$$UO_2{<}^{OH}_{OH} + {}^{HO.NO_2}_{HO.NO_2} = UO_2{<}^{O.NO_2}_{O.NO_2} + 2H_2O.$$

They are derived from the acids by replacing the hydrogen by uranyl, $UO_2$, which is bivalent.—*Uranyl nitrate*, $UO_2(NO_3)_2$, is easily obtained, as above described, and crystallizes well in lemon-yellow prisms.—*Uranyl sulphate*, $UO_2(SO_4)$, is formed by treating the nitrate with

sulphuric acid. It combines with ammonium sulphate, forming the salt $UO_2(SO_4) + (NH_4)_2SO_4 + 2H_2O$, which is difficultly soluble in water and crystallizes in lemon-yellow prisms.

**Uranates.**—When a uranyl salt is treated with a soluble hydroxide a precipitate is formed which is a salt of an acid, $H_2U_2O_7$, which may be called *diuranic acid*, as in composition it is analogous to dichromic and disulphuric acids.

*Sodium diuranate*, $Na_2U_2O_7$, is a fine yellow powder, and is manufactured and sold under the name *uranium yellow*, being used as a pigment for coloring glass, etc.—*Ammonium diuranate*, $(NH_4)_2U_2O_7$, is also manufactured on the large scale. When it is treated with a solution of ammonium carbonate it dissolves, and from the solution a salt of the composition $UO_2(CO_3) + 2(NH_4)_2CO_3$ crystallizes out. The solubility of ammonium diuranate in ammonium carbonate is utilized in analysis.—The oxide of the formula $U_3O_8$ above referred to may be a uranous salt of uranic acid as represented by the formula

$$\left. \begin{array}{l} UO_2{<}^O_O \\ UO_2{<}^O_O \end{array} \right\} U.$$

Many uranium salts exhibit in solution a beautiful fluorescence.

# CHAPTER XXXII.

**General.**—At the close of Chapter XII (which see), which treated of the elements of Family VII, Group B, or the chlorine group, reference was made to manganese, and attention was called to the fact that in some respects it resembles chlorine. The resemblance is seen in the formation of an oxide, $Mn_2O_7$, and an acid, $HMnO_4$, analogous to perchloric acid. On the other hand, in many of its compounds it plays the part of a base-forming element, and in this capacity it forms two series of compounds, known as the *manganous* and the *manganic* compounds. In the former the element appears to be bivalent, and in the latter trivalent. The formulas of some of the principal manganous compounds are :

$$MnCl_2, \ Mn(OH)_2, \ MnO, \ Mn(NO_3)_2, \ MnSO_4, \ MnCO_3, \text{ etc.}$$

The formulas of some of the principal manganic compounds are :

$$Mn(OH)_3, \ Mn_2O_3, \ MnO(OH), \ Mn_2(SO_4)_3, \ KMn(SO_4)_2 + 12H_2O, \text{ etc.}$$

These two series of compounds are analogous in composition to the chromous and chromic compounds, but, while the chromic compounds are more stable than the chromous compounds, the manganous compounds are more stable than the manganic compounds. By contact with the air, the manganous are not as a rule converted into the manganic compounds.

Corresponding to chromic acid, there is a *manganic acid*, $H_2MnO_4$ ; and, further, there is the *permanganic acid* already mentioned, of the formula $HMnO_4$. An analogous compound of chromium, perchromic acid, $HCrO_4$,

is believed to be formed when hydrogen peroxide is added to an aqueous solution of chromic acid, but this is by no means certain. Manganic acid and its salts are very unstable, and are readily converted into permanganic acid and the permanganates. On the other hand, perchromic acid, if it exists at all, is spontaneously decomposed, yielding ordinary chromic acid. To sum up, then, both chromium and manganese form four classes of compounds. But, while chromium under ordinary circumstances preferably forms chromic salts and salts of chromic acid, manganese preferably forms manganous salts and salts of permanganic acid.

Manganese forms a number of oxides corresponding to the formulas $MnO$, $Mn_2O_3$, $Mn_3O_4$, $MnO_2$, and $Mn_2O_7$. Of these probably the one of the composition $Mn_3O_4$ and perhaps that of the composition $Mn_2O_3$ are compounds of the others, as will be pointed out further on.

**Forms in which Manganese occurs in Nature.**—The principal natural compound of manganese is the black oxide or pyrolusite, $MnO_2$. Besides this, however, there are several compounds found in nature, the principal ones being, braunite, $Mn_2O_3$, hausmannite, $Mn_3O_4$, manganite, $Mn_2O_2(OH)_2$, and rhodocroisite, which is the carbonate, $MnCO_3$.

**Preparation and Properties.**—The metal is isolated from its oxides by heating them to a high temperature with charcoal. It looks like cast iron, is brittle and hard, and has the specific gravity 8. It easily becomes oxidized in the air, decomposes warm water, and dissolves readily in dilute acids. It is used as a constituent of some useful alloys, and imparts certain desirable properties to iron, as will be pointed out when that metal is taken up.

**Manganous Chloride, $MnCl_2$.**—This chloride is obtained in solution by dissolving any one of the oxides or hydroxides or the carbonate of manganese in hydrochloric acid with the aid of gentle heat. Its formation in the preparation of chlorine from manganese dioxide and hydrochloric acid was referred to under Chlorine (which see). When the solution is evaporated to the proper

concentration, the salt crystallizes out in pink, mono-clinic plates of the composition $MnCl_2 + 4H_2O$. When the crystallized salt is heated, it decomposes into the oxide and hydrochloric acid, as so many other chlorides do. It forms double chlorides, an example of which is the ammonium compound of the formula $MnCl_2.2NH_4Cl$ or $(NH_4)_2MnCl_4$.

When manganic hydroxide, $Mn(OH)_3$, is treated in the cold with hydrochloric acid, a deep brown-colored solution is formed, which is believed to contain the *trichloride*, $MnCl_3$. On standing, however, this solution gives off chlorine slowly, and when heated it gives it off rapidly, and the color changes to pink when only manganous chloride is left in the solution.

Phenomena similar to those just mentioned are observed when manganese dioxide is treated with hydrochloric acid in the cold, and it is believed that the *tetrachloride*, $MnCl_4$, is contained in the solution.

While the *tetrafluoride* itself has not been isolated, a solution is obtained by treating manganese dioxide with concentrated hydrofluoric acid which with potassium fluoride gives a salt of the formula $MnF_4.2KF$ or $K_2MnF_6$.

**General Remarks Concerning the Oxides.**—The series of oxides of manganese strongly suggests that of the oxides of lead. Manganese, however, forms one oxide, the heptoxide, $Mn_2O_7$, for which there is no analogue among the compounds of lead. Placing the formulas of the oxides of the two metals side by side, we have the following table:

| | |
|---|---|
| PbO | MnO |
| $Pb_2O_3$ | $Mn_2O_3$ |
| $Pb_3O_4$ | $Mn_3O_4$ |
| $PbO_2$ | $MnO_2$ |
| | $Mn_2O_7$. |

Just as lead oxide when heated is converted into red-lead, $Pb_3O_4$, so the other oxides of manganese are converted into the oxide, $Mn_3O_4$, when heated. This has already been seen in the preparation of oxygen by heating the dioxide. In the same way, the oxide, $Mn_2O_3$, loses

enough oxygen, and the lowest oxide, MnO, takes up enough to form the same product:

$$3Mn_2O_3 = 2Mn_3O_4 + O \; ;$$
$$3MnO + O = Mn_3O_4.$$

When treated with energetic oxidizing agents in the presence of the alkalies, all the oxides are converted into manganates. On the other hand, if a manganate is reduced in the presence of an acid the tendency to form manganous compounds shows itself, and all oxygen present in excess of that required to form the manganous salt is given off.

**Manganous Oxide, MnO,** is formed by reducing one of the higher oxides in a current of hydrogen.

**Manganous Hydroxide, Mn(OH)₂,** is formed as a white precipitate when a soluble hydroxide is added to a solution of a manganous salt. Suspended in the alkali, or in contact with air, it absorbs oxygen, and is converted into hydroxides corresponding to the higher oxides.

**Manganous-manganic Oxide, Mn₃O₄,** occurs in nature as the mineral hausmannite. It is formed, as already stated, by igniting the other oxides in contact with the air. When heated with dilute nitric acid, it acts like the corresponding oxide of lead, giving manganous nitrate, and leaving manganese dioxide:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

It breaks down in the same way with dilute sulphuric acid. These facts make it appear probable that the oxide is the manganous salt of normal manganous acid, $Mn(OH)_4$, just as minium or red lead is regarded as the lead salt of normal plumbic acid, $Pb(OH)_4$, (p. 651.) This view is expressed by the formula $Mn\begin{cases} O \\ O \end{cases}>Mn \\ \begin{cases} O \\ O \end{cases}>Mn$. The decomposition with acids, as with sulphuric acid, would, according to this, be represented thus:

$$MnO_4Mn_2 + 2H_2SO_4 = 2MnSO_4 + Mn(OH)_4.$$

The hydroxide thus formed would then break down into the dioxide and water.

**Manganic Oxide, Mn₂O₃,** occurs in nature as the mineral braunite, and it can be made from the other oxides by igniting them in oxygen. A hydroxide related to this, and having the composition MnO.OH, analogous to the compounds of aluminium and chromium of the formulas AlO.OH and CrO.OH, is found in nature, and is known as manganite. The hydroxide, Mn(OH)₃, is formed when manganous hydroxide, Mn(OH)₂, is exposed in a solution of ammonia in contact with the air, and forms a brownish black powder.

**Manganese Dioxide, MnO₂.**—This important compound occurs in nature in very considerable quantities, and is known as pyrolusite or the black oxide of manganese. It is obtained artificially by gently igniting manganous nitrate. A hydroxide derived from the dioxide is obtained by treating a manganous salt in alkaline solution with a soluble hypochlorite or chlorine or bromine. The chief application of the dioxide is in the preparation of chlorine, for which purpose it is used in large quantities. It is also used for making oxygen, and for the purpose of decolorizing glass. In the last process a small quantity is added to the molten glass. This alone would give the glass an amethyst color. Without it the glass would be green. One color counteracts the other, and the glass appears colorless. As regards the action of hydrochloric acid upon manganese dioxide, it has been suggested, upon the basis of experimental investigations, that the first product of the action is a compound of the formula H₂MnCl₆, which is the chlorine compound analogous to the oxygen acid, H₂MnO₃. The action is supposed to take place as represented in the following equation:

$$O{=}Mn{=}O + 6HCl = \begin{matrix} H-(Cl_2) \\ H-(Cl_2) \end{matrix}{>}Mn{=}Cl_2 + 2H_2O.$$

The suggestion is made, further, that it is this compound, and not manganese tetrachloride, MnCl₄, which breaks down yielding chlorine, the action taking place thus:

$$\begin{matrix} H-(Cl_2) \\ H-(Cl_2) \end{matrix}{>}MnCl_2 = MnCl_2 + 2HCl + Cl_2.$$

The manganous chloride and some of the chlormanganous acid then react, forming a compound which with water undergoes decomposition. In regard to this suggestion, it can only be said that as yet it is not sufficiently supported by facts. The formation of the unstable compound, $H_2MnCl_6$, appears highly probable, however, in view of the conduct of so many other chlorides in the presence of hydrochloric acid.

**Manganites.**—There are some salts known as the *manganites*, which are clearly derived from hydroxides related to manganese dioxide. Theoretically the simplest hydroxides of this kind are those of the formulas $Mn(OH)_4$ and $MnO(OH)_2$. The salts are not, however, derived from these, but from more complicated forms, as $H_2Mn_2O_5$ and $H_2Mn_5O_{11}$, the relations between which and the simpler hydroxides are shown in the equations

$$2MnO(OH)_2 = Mn_2O_3(OH)_2 + H_2O\ ;$$
$$5MnO(OH)_2 = Mn_5O_9(OH)_2 + 4H_2O.$$

The potassium salt, $K_2Mn_5O_{11}$, is obtained when carbon dioxide is conducted into a solution of potassium manganate. Further, a salt of the composition $KH_3Mn_4O_{10}$ is formed as a brown insoluble powder by boiling the other manganites with potassium hydroxide or carbonate.

**Weldon's Process for the Regeneration of Manganese Dioxide in the Preparation of Chlorine.**—Under the head of Chlorine (which see), Weldon's process was referred to; but as a satisfactory explanation of the working of the process could not be given without dealing with some rather complicated compounds of manganese, a fuller account was postponed until these compounds should be taken up. The object in view is to utilize the waste liquors from the chlorine factories. When manganese dioxide is treated with hydrochloric acid, as we have seen, manganous chloride and chlorine are formed, according to the equation

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The manganous chloride was of no special value until it was shown that by a comparatively simple method it can be converted into a compound which with hydrochloric acid gives chlorine. When it is treated in solution with lime the corresponding hydroxide is precipitated:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2;$$

and when this hydroxide mixed with lime is allowed to stand exposed to the air oxidation takes place, and a compound $CaMnO_3$ or $CaMn_2O_5$ is formed:

$$Mn(OH)_2 + Ca(OH)_2 + O = CaMnO_3 + 2H_2O;$$
$$2Mn(OH)_2 + Ca(OH)_2 + 2O = CaMn_2O_5 + 3H_2O.$$

These compounds give chlorine when treated with hydrochloric acid. They may indeed be regarded as consisting of lime and manganese dioxide, $CaO.MnO_2$ and $CaO.2MnO_2$, and the action of hydrochloric acid takes place thus:

$$CaO.MnO_2 + 6HCl = CaCl_2 + MnCl_2 + 3H_2O + Cl_2;$$
$$CaO.2MnO_2 + 10HCl = CaCl_2 + 2MnCl_2 + 5H_2O + 2Cl_2.$$

In practice, the waste liquor is mixed with calcium carbonate in order to neutralize the acid. After settling, lime enough is added to precipitate the manganese as hydroxide, and to form with this a mixture in molecular proportions. Into this mixture steam and air are passed, when the oxidation referred to takes place, and calcium manganite is formed.

**Sulphides.**—When a solution of a manganous salt is treated with ammonium sulphide, a flesh-colored precipitate, which is thought to be the hydrosulphide, is formed. When this is exposed to the air it turns dark in consequence of oxidation; and if allowed to stand in the liquid, if this is concentrated, it turns green and becomes crystalline. The product thus formed is manganous sulphide, $MnS$. This also occurs in nature as alabandite. A disulphide, $MnS_2$, corresponding to the dioxide is also found in nature, and is known as hauerite.

**Manganous Cyanide, Mn(CN)₂**, in combination with potassium or sodium cyanide as the compounds $Mn(CN)_2.$ $4KCN$ or $K_4Mn(CN)_6$, and $Mn(CN)_2.4NaCN$ or $Na_4Mn(CN)_6$, is formed by treating solutions of manganous salts with potassium or sodium cyanides. When exposed to the air, or when the solutions are boiled, salts of the formulas $Mn(CN)_3.3KCN$ or $K_3Mn(CN)_6$ and $Mn(CN)_3.3NaCN$ or $Na_3Mn(CN)_6$ are formed.

**Manganous Carbonate, MnCO₃**, is found in nature, and is precipitated when a solution of a manganous salt is treated with a soluble carbonate.

**Manganous Sulphate, MnSO₄**, is formed by heating the oxides of manganese with concentrated sulphuric acid. If higher oxides than manganous oxide are used, oxygen is given off:

$$MnO \ + H_2SO_4 \ = MnSO_4 \ + H_2O \ ;$$
$$Mn_2O_3 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O \ ;$$
$$MnO_2 \ + H_2SO_4 \ = MnSO_4 \ + H_2O \ + O.$$

It crystallizes at low temperatures with seven molecules of water, and at ordinary temperatures with five, in this respect resembling cupric sulphate (which see). The salt of the formula $MnSO_4 + 7H_2O$ forms bright-red monoclinic prisms; while that of the formula $MnSO_4 + 5H_2O$ forms pink triclinic crystals. Between 20° and 30° it forms monoclinic prisms with four molecules of water.

**Manganic Sulphate, Mn₂(SO₄)₃**, is formed when the oxide $Mn_3O_4$, or the finely divided precipitated dioxide, $MnO_2$, is treated with sulphuric acid at not too high a temperature. It forms a dark green amorphous powder, which is easily decomposed by heat and by water. With the sulphates of the alkali metals it forms salts analogous to the alums, as $KMn(SO_4)_2 + 12H_2O$ and $NH_4Mn(SO_4)_2 + 12H_2O$, in which manganese takes the place of aluminium. This fact makes it appear probable that in the manganic compounds manganese is trivalent, as aluminium probably is in its compounds.

**Manganic Acid and the Manganates.**—When an oxide of manganese is treated with an energetic oxidizing agent in the presence of a strong base it is converted into a

manganate, just as the oxides of chromium are converted into chromates and the compounds of sulphur into sulphates. These three classes of compounds are analogous as far as the composition is concerned, as shown by the formulas

$$M_2MnO_4 \qquad\qquad M_2CrO_4 \qquad\qquad M_2SO_4$$
Manganate            Chromate            Sulphate

The manganates are, however, quite unstable except in alkaline solution, and when they decompose they form the permanganates.—*Potassium manganate*, $K_2MnO_4$, is formed by fusing manganese dioxide with potassium hydroxide, when, if the air is not in contact with the mass, the reaction takes place as represented in the equation

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

It is also made by fusing the dioxide with potassium hydroxide and potassium chlorate, when this reaction takes place :

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

When the mass obtained in either way is treated with water a dark-green solution of the manganate is formed, and by allowing this to evaporate at the ordinary temperature in a partial vacuum, or in an atmosphere free of oxygen, the salt is obtained in small crystals, which are almost black. When a solution of a manganate is treated with an acid, the manganic acid is at once decomposed into permanganic acid and manganese dioxide :

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O.$$

The change of a manganate to a permanganate is effected simply by passing carbon dioxide into the solution, or by boiling or allowing the solution to stand in the air. The change by means of carbon dioxide is represented by the equation

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + MnO_2 + 2KMnO_4.$$

With water the change takes place thus:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

The potassium hydroxide and the manganese dioxide react upon each other to form a manganite of more or less complicated composition. While the manganates are decomposed by acids, forming permanganates, the latter are decomposed by alkalies, forming manganates. Thus, when a solution of potassium permanganate is boiled with potassium hydroxide the color changes to green, owing to the formation of the manganate:

$$2KOH + 2KMnO_4 = 2K_2MnO_4 + H_2O + O.$$

This change takes place readily in the presence of substances which have the power to take up oxygen; but if such substances are present the reduction goes further, forming finally a manganite which is a derivative of the hydroxide, $MnO(OH)_2$.

**Permanganic Acid and the Permanganates.**—The simplest method of obtaining the permanganates is by decomposition of the manganates, as described in the last paragraph.

**Potassium Permanganate, $KMnO_4$,** is manufactured on the large scale by oxidizing manganese dioxide in the presence of a base. Sometimes the oxidation is effected by the oxygen of the air; sometimes by the action of an oxidizing agent, as potassium chlorate or nitrate. The fundamental reaction in each case is that represented by the equation

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O.$$

As will be observed, it is a reaction of the same kind as that involved in the conversion of a sulphite into a sulphate. Probably the first action of the hydroxide upon the dioxide consists in the formation of the manganite, $K_2MnO_3$, and this is then oxidized to the manganate. When the solution of the manganate is treated with sulphuric acid a change similar to those referred to above takes place, and the permanganate is formed. The salt

is easily soluble in water, and is deposited from its solution in crystals, isomorphous with potassium perchlorate, which appear nearly black, with a greenish lustre. Its solution in water has a purple or reddish-purple color, according to the concentration. Very concentrated solutions appear almost black. The salt is used extensively in the laboratory and in the arts as an oxidizing agent. Its action will be readily understood from what has already been said in regard to the conduct of manganese towards acids and towards alkalies. When the permanganate undergoes decomposition in the presence of an acid the manganese tends to form a manganous salt, and all the oxygen present in excess of what is needed for this purpose is given off. Thus the decomposition with sulphuric acid takes place as represented in the equation

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O.$$

Therefore, when potassium permanganate is used as an oxidizing agent in acid solution, two molecules of the salt $KMnO_4$ give five atoms of oxygen. On the other hand, when the action takes place in alkaline solution the action reaches its limit in a manganite, which, for purposes of calculation, may be regarded as having the composition $K_2MnO_3$. The first change is from the permanganate to the manganate as represented in the equation

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O,$$

and then the manganate loses another atom of oxygen,

$$2K_2MnO_4 = 2K_2MnO_3 + 2O.$$

Therefore, when the permanganate is used as an oxidizing agent in alkaline solution, two molecules of the salt yield three atoms of oxygen.

The permanganates and maganates are valuable disinfecting agents, and the sodium salts are extensively used for this purpose, under the name of *Condy's liquid.*

When a solution of barium permanganate is treated with sulphuric acid, free permanganic acid is obtained

in solution. It is extremely unstable, and decomposes spontaneously when the solution is exposed to the light or is heated. When dry potassium permanganate is added to concentrated sulphuric acid, oily drops separate and collect upon the bottom of the vessel. These are *manganese heptoxide*, $Mn_2O_7$, which is formed thus:

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + Mn_2O_7 + H_2O.$$

The compound bears to permanganic acid the relation of an anhydride:

$$2HMnO_4 = Mn_2O_7 + H_2O.$$

It is extremely unstable, giving off oxygen with great ease, and therefore acting as a powerful oxidizing agent.

As regards the constitution of the manganates and permanganates, they are respectively regarded as analogous to the sulphates and perchlorates. Accordingly manganic acid is represented by the formula
$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Mn}}-OH \text{ or } MnO_2(OH)_2,$$ while permanganic acid is

represented by the formula $O=\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Mn}}-OH$ or $MnO_3(OH)$.

**Reactions which are of Special Value in Chemical Analysis.**—The conduct of manganous salts towards *soluble hydroxides* and towards *soluble carbonates* has been described. The hydroxide is soluble in ammonia and ammonium salts, but this solution turns brown when exposed to the air and the manganese is gradually precipitated as the hydroxide $Mn(OH)_3$.

The conduct towards *ammonium sulphide* has been described. When *oxidizing agents* like *hypochlorites, chlorine,* or *bromine* act upon manganous salts in solutions in presence of soluble hydroxides, hydroxides corresponding to the dioxide $MnO_2$, such as $Mn(OH)_4$, $MnO(OH)_2$, are precipitated. Instead of the above-

mentioned oxidizing agents, *potassium permanganate* may be used.

The action of potassium permanganate and manganate as oxidizing agents when used in alkaline and in acid solutions has been described above.

Manganese is easily detected by heating the substance under examination with *nitric acid* and *lead peroxide*, when permanganic acid will be formed if manganese is present, and its formation will be shown by the purple color of the solution.

With *microcosmic salt* and *borax* manganese gives an amethyst-colored bead in the oxidizing flame, which becomes colorless in the reducing flame.

# CHAPTER XXXIII.

**General.**—The three elements which form this group are in many respects very similar, and their atomic weights differ but little from one another. That of iron (55.6) is nearly the same as that of manganese (54.57), while cobalt and nickel have nearly the same atomic weight. There is much in iron which suggests manganese. It forms two series of compounds, the *ferrous* and *ferric* compounds, which are analogous to the *manganous* and *manganic* compounds. In the first series iron appears to be bivalent, as shown in the formulas

$$FeCl_2, \ Fe(OH)_2, \ FeO, \ FeS, \ FeSO_4, \ FeCO_3, \ etc.$$

In the second series it appears to be trivalent, as indicated in the formulas

$$FeCl_3, \ Fe(OH)_3, \ Fe_2O_3, \ Fe(NO_3)_3, \ Fe_2(SO_4)_3, \ etc.$$

Like chromium and manganese it also forms an acid known as *ferric acid*, $H_2FeO_4$, which in composition is analogous to chromic and manganic acids. The soluble salts of this acid are, however, unstable, and on decomposing yield ferric hydroxide. Oxidizing agents readily convert ferrous compounds into ferric compounds, and reducing agents reconvert the latter into the former. When exposed to the air most ferrous compounds are oxidized to ferric compounds. The ferrous compounds in which iron is bivalent are similar to the compounds of the zinc group. The ferric compounds, however, in which the iron is trivalent, are similar to the aluminium compounds ; and in ferric acid it exhibits a resemblance to chromium. Cobalt and nickel resemble iron in re-

spect to their power to form two series of compounds corresponding to the ferrous and ferric compounds. Both elements preferably form compounds of the lower series, examples of which are represented by the formulas

$$CoCl_2 \quad Co(OH)_2 \quad CoO \quad Co(NO_3)_2 \quad CoSO_4 \quad \text{etc.}$$
$$NiCl_2 \quad Ni(OH)_2 \quad NiO \quad Ni(NO_3)_2 \quad NiSO_4 \quad \text{etc.}$$

Cobalt forms a few compounds corresponding to the ferric series; and nickel forms a hydroxide, of the formula $Ni(OH)_3$. While the power of cobalt to form compounds in which it is trivalent is much weaker than that of iron, it is stronger than that of nickel, the latter being almost exclusively bivalent. In general terms, it may be said that manganese forms a greater variety of compounds than any other element except carbon. In the manganous compounds it exhibits analogies with zinc, copper, and some other bivalent elements; in the manganic compounds it exhibits analogies with aluminium; in manganic acid it suggests sulphur and chromium; and in permanganic acid it suggests chlorine. In the following table some of the analogies which are plainly discernible between the elements mentioned, and iron, cobalt, and nickel, are indicated. The formulas of those compounds which are not easily obtained, and are exceptional, are put in brackets :

| | | | | | |
|---|---|---|---|---|---|
| $MnSO_4$ | $[Mn_2(SO_4)_3]$ | $MnO_2$ | —— | $K_2MnO_4$ | $KMnO_4$ |
| $[CrSO_4]$ | $Cr_2(SO_4)_3$ | —— | $CrO_3$ | $K_2CrO_4$ | $[HCrO_4](?)$ |
| $FeSO_4$ | $Fe_2(SO_4)_3$ | —— | —— | $[K_2FeO_4]$ | |
| $CoSO_4$ | $Co(OH)_3$ | —— | —— | —— | —— |
| $NiSO_4$ | $[Ni(OH)_3]$ | —— | —— | —— | —— |
| —— | $Al_2(SO_4)_3$ | —— | —— | —— | —— |
| $ZnSO_4$ | —— | —— | —— | —— | —— |
| —— | —— | $SO_2$ | $SO_3$ | $K_2SO_4$ | —— |
| —— | —— | —— | —— | —— | $KClO_4$ |

As regards the question whether the formula of the simpler ferric compounds is to be written with two atoms of iron in every case, it is in much the same state as the question in regard to aluminic compounds. Is ferric chloride $FeCl_3$ or $Fe_2Cl_6$? A determination of the

specific gravity of the vapor gave a result in accordance
with the larger formula, but this would not appear to be
sufficient evidence in view of the peculiar results ob-
tained with aluminium chloride. Considering the close
resemblance between ferric compounds and the com-
pounds of aluminium, it seems probable that, if alu-
minium is trivalent, iron is also trivalent in these com-
pounds. The ease with which ferric chloride forms com-
pounds with other chlorides suggests, further, that the
compound of the simpler formula $FeCl_3$ may combine
with another molecule of the same kind to form a double

chloride of the formula $Fe_2Cl_6$ or $Fe{\large\diagup}{\Large\diagdown}\begin{matrix}(Cl_2)\\(Cl_2)\\(Cl_2)\end{matrix}{\large\diagdown}{\Large\diagup}Fe$. It may

be objected to this that it is not probable that such a
compound could be converted into vapor without under-
going decomposition, and, according to the one determi-
nation of the specific gravity, it does not appear to
undergo decomposition. What value to attach to this
objection it is impossible to say at present. In any case,
a further knowledge of the facts is needed before a final
conclusion can be reached. In the mean time it seems
to be justifiable to consider iron trivalent in ferric com-
pounds, as aluminium is considered trivalent in its com-
pounds, chromium in chromic compounds, and manga-
nese in manganic compounds.

That iron is bivalent in ferrous compounds is probable
from the analogy of these compounds with the distinctly
bivalent metals, like copper, zinc, etc. Further, a deter-
mination of the specific gravity of the vapor of ferrous
chloride gave a figure which indicated that the vapor
consisted of about an equal number of molecules of the
formulas $FeCl_2$ and $Fe_2Cl_4$, so that it appears that at a
lower temperature the compound has the formula $Fe_2Cl_4$,
and that the compound breaks down or dissociates, form-
ing the simpler compound. This subject requires further
investigation. In the mean time the simpler formula will
be used, as it probably represents the chemical molecule
or that smallest particle of the compound which comes
into play in chemical reactions. If iron is bivalent in

ferrous compounds, then in all probability cobalt and nickel are bivalent in their principal compounds.

## Iron, Fe (At. Wt. 55.6).

**Introductory.**—The importance of this metal to mankind can hardly be overestimated, and for many centuries it has played a commanding part in the industries. It requires little thought to convince one that without it the earth would be quite a different place from what it now is. In the earliest periods of history metals were but little used, as but few of them are furnished ready for use by nature. Stones were therefore first used, and these were shaped into a variety of implements, many of which still exist, and furnish evidence of the Stone Age. After a time copper and tin were used in the form of an alloy or bronze, as copper is found in nature in the free condition. During this period, known as the Bronze Age, stone implements gave way to those made of bronze. Afterwards men learned to extract iron from its ores, and the Iron Age was introduced ; and this has continued up to the present, as nothing has since been found which can advantageously take the place of iron. The suggestion has been made that as it is less difficult to extract iron from its ores than to make bronze, possibly iron was used as early as bronze—perhaps earlier, but that, owing to the fact that iron easily rusts, implements of this metal have disappeared, while those made of bronze remain intact.

**Forms in which Iron occurs in Nature.**—Iron occurs in small quantity native in meteorites, in the basalts of Bohemia and Greenland, and in some gabbros. The iron meteorites always contain nickel, and frequently small quantities of other elements, as manganese and carbon. Compounds of iron occur in enormous quantities, and widely distributed in the earth. Among the more important are the following-named : hematite, $Fe_2O_3$ ; magnetite, $Fe_3O_4$ ; brown iron ore, $Fe_4O_3(OH)_6$ ; siderite, or the carbonate, $FeCO_3$ ; pyrite, $FeS_2$ ; pyrrhotite, $Fe_7S_8$. It is also contained in many silicates in small quantity, and in consequence of the disintegration of the

constituents of rocks it is found in the soil, and in many natural waters. In the vegetable kingdom it is always found in chlorophyll, and in the animal kingdom always in the blood. The compounds which are chiefly used for the purpose of making iron, or the iron ores, are magnetite, $Fe_3O_4$; hematite, $Fe_2O_3$; brown iron ore, $Fe_4O_3(OH)_6$; and spathic iron, or siderite, $FeCO_3$.

**Metallurgy.**—The ores of iron, after they are broken up, are first roasted, in order to drive off water from the hydroxides; to decompose carbonates; to oxidize sulphides; and, as far as possible, to convert the oxides into ferric oxide, $Fe_2O_3$, which is the most easily reducible of the oxides of iron. After the ores are prepared in this way they are reduced by heating them with carbon and fluxes in the blast-furnaces, when the iron collects in the molten condition under the so-called slag at the bottom of the furnace. Blast-furnaces differ somewhat in construction, but the essential parts are represented in Fig. 14.

The inner cavity of the furnace is narrow at the top and bottom, as is shown in the figure. Through pipes, known as *tuyeres*, such as that represented at the lower part of the left-hand side of the figure, air is blown into the furnace to facilitate the combustion. In modern furnaces arrangements are made above for carrying off the gases



Fig. 14.

and utilizing them as fuel. The inner walls are built of fire-bricks, and these are surrounded by ordinary bricks, or stone-work. The furnaces vary in height from 25 to 80 or 90 feet, an average height being about 45 feet. The reduction of the ores is accomplished by placing in the furnace alternating layers of coke or charcoal, and the ores mixed with proper fluxes. The

nature of the flux depends upon the ore. If this contains silicon dioxide or clay, lime is added; while, if it contains considerable lime, minerals rich in silicic acid are used, such as feldspar, clay-slate, etc. The object of the flux is to form a slag in which the reduced iron collects, and by which it is protected from oxidation. When the fire is once started in a blast-furnace the operation of reduction is continuous until the furnace is burned out. Alternate layers of ore and flux and carbon are added, and, as the reduced iron collects below, it is from time to time drawn off and allowed to solidify in moulds of sand. The operation requires close attention. The ores must be carefully studied, and the nature and amount of flux regulated according to the character of the ore as above stated. Then, too, the temperature of the furnace is a matter of importance, and must be watched, and regulated by means of the blast. The reduction is largely accomplished by carbon monoxide. In the lower part of the furnace the fuel burns to carbon dioxide, but this comes in contact with hot carbon, and is then reduced to the monoxide. The hot monoxide in contact with the oxides of iron reduces these, and is itself converted into the dioxide. A large proportion of the carbon monoxide, however, escapes oxidation, and this is carried off from the top of the furnace to the bottom by properly arranged pipes, and is then utilized as fuel. A furnace lasts from two to twenty years, and sometimes longer.

**Varieties of Iron.**—The iron obtained as above described is known as *pig-iron* or *cast-iron*. It is very impure, containing carbon, phosphorus, sulphur, silicon, etc. If, when drawn from the furnace, the iron is cooled rapidly, nearly all the carbon contained in it remains in chemical combination, and the iron has a silver-white color. This product is known as *white cast-iron*. If the iron cools slowly, most of the carbon separates as graphite, and this being distributed through the mass gives it a gray color. This product is known as *gray cast-iron.* If the ore contains considerable manganese, this is reduced with the iron, and iron made from such ores and

containing manganese has the power to take up more carbon than ordinary iron. This product, containing from 3.5 to 6 per cent combined carbon, is known as *spiegel-iron.*

All varieties of cast-iron are brittle, and easily fusible. The gray iron fuses at a lower temperature than the white, and is not as brittle; it is therefore well adapted to making castings. When cast-iron is treated with hydrochloric acid the carbon which is present in combined form is given off in combination with hydrogen as hydrocarbons, some of which have a disagreeable odor. This is, of course, the cause of the bad odor noticed in dissolving ordinary cast-iron in acids. The uncombined or graphitic carbon, on the other hand, remains undissolved. Owing to its brittleness, cast-iron cannot be welded. When the carbon, silicon, and phosphorus are removed the iron becomes tough and malleable, and its melting-point is much raised. The product thus obtained is known as *wrought-iron.*

*Puddling.*—Wrought-iron is obtained from cast-iron by the puddling process. The puddling furnace has a flat, oval hearth, and low arched roof. The sides of the hearth are lined with a layer of iron ore (oxide). Coal is burned on a grate and the flame passes into the furnace at one end and out at the other, thus coming in contact with the roof and the charge of iron. By contact with the flame, and by the heat radiated from the roof, the cast-iron melts. The carbon and silicon are removed from the molten cast-iron, partly by the oxygen in the air or flame, but principally by the oxygen in the iron ore, which is itself thus reduced to wrought-iron.

Wrought-iron contains less than 0.6 per cent of carbon, and, as the percentage of carbon decreases, the malleability increases and the melting-point rises. The melting-point of good wrought-iron is from 1900° to 2100°. Small quantities of sulphur, phosphorus, silicon, and manganese exert a very marked influence upon its properties. The process of welding consists in heating

two pieces of iron to a high temperature, putting some borax upon one of them, laying them together, and hammering, when, as is well known, they adhere firmly together. The object of the borax is to keep the surfaces bright, which it does by uniting with the oxide and forming an easily fusible borate.

*Bessemer Process.*—Molten cast-iron is poured into a large vessel called the converter. The carbon and silicon are entirely oxidized and removed by means of a blast of air forced through the metal from below. No fuel is used, as the heat generated by the oxidation of carbon and silicon is sufficient to raise the temperature above 2100°. The converter contains molten wrought-iron after the oxidation. By addition of spiegel-iron **a** product containing any desired percentage of carbon is obtained.

Iron which contains more than a very small percentage of phosphorus is not adapted to the manufacture of Bessemer steel in the ordinary way; but it has been found that, if the converters are lined with lime and magnesia, such iron may be used. Under these circumstances the phosphorus is oxidized, and forms calcium and magnesium phosphates, which are of value as fertilizers (see Calcium Phosphate). This process is known as the Thomas-Gilchrist or the basic-lining process.

*Siemens-Martin Furnace.*—This is simply a reversible puddling furnace in which gas is used as fuel. The gas is previously heated in a Siemens regenerative furnace.

*Steel and Wrought-iron.*—The product of the puddling furnace is called wrought-iron; while those formed in the Bessemer process and in the Siemens-Martin furnace are called *steel*. Bessemer steel often contains less than 0.6 per cent of carbon, and Siemens-Martin steel is the purest form of wrought-iron, containing less carbon and silicon than the product of the puddling furnace.

*Tempering.*—When steel is heated and cooled suddenly, it is rendered extremely hard and brittle; and when hardened steel is carefully heated, and allowed to

cool slowly, it becomes very elastic. This process is called tempering.

**Properties of Iron.**—Pure iron is almost unknown. Of the commercial varieties, it follows from what has been said that wrought-iron is the purest. That which is used for piano-strings is the purest iron which can be bought; it contains only about 0.3 per cent of impurities. Pure iron can be made in the laboratory by igniting the oxide or oxalate in a current of hydrogen, and by reducing ferrous chloride in hydrogen. In larger quantity it can be prepared by melting the purest wrought-iron in a lime crucible by means of the oxyhydrogen flame. The impurities are taken up by the crucible, and a regulus of the pure metal is left behind. That made by reduction of the oxide or oxalate is, of course, in finely divided condition. If in its preparation the temperature is kept as low as possible, the product takes fire when brought in contact with the air; while if the temperature is high, the product has not this power. Iron is white, and is one of the hardest metals; and its melting-point is higher than that of wrought-iron. Pure iron is attracted by the magnet. In contact with a magnet, or when placed in a coil through which an electric current is passing, it becomes a magnet; but the purer it is the sooner it loses the magnetic power when removed from the magnet or the coil. Steel, however, retains its magnetism. When heated to a sufficiently high temperature iron burns, and forms the oxide, $Fe_3O_4$. This takes place much more easily in oxygen than in the air. In dry air iron does not undergo change, but in moist air it *rusts*, or it becomes covered with a layer of oxide and hydroxide, which is formed by the action of the air, carbon dioxide, and water. Water that contains salts in solution facilitates the rusting. Various methods are adopted to protect iron from this change, most of which are, however, purely mechanical. A method which promises valuable results is that invented by Barff, which consists in introducing the iron into water vapor at a temperature of 650°, when it becomes covered with a firmly adhering layer of oxide.

Iron dissolves in acids with evolution of hydrogen, and generally with formation of ferrous salts :

$$Fe + 2HCl = FeCl_2 + H_2 ;$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

When cold nitric acid is used, ferrous nitrate and ammonium nitrate are the products ; if the acid is warmed, ferric nitrate and oxides of nitrogen are formed. When an iron wire which has been carefully polished is introduced for an instant into red fuming nitric acid it can afterward be put into ordinary nitric acid without undergoing change. It is said to be in the passive state ; and the commonly accepted explanation of the phenomenon is, that the wire is covered with a thin layer of oxide. As, however, the passive condition is lost by contact with an ordinary wire, the explanation does not appear to be adequate.

**Ferrous Chloride, $FeCl_2$.**—When iron is dissolved in hydrochloric acid without access of air, and the solution evaporated, crystals of the composition $FeCl_2 + 4H_2O$ are obtained. When heated for the purpose of driving off the water, the crystallized compound decomposes. The dry chloride can be obtained by heating iron in a current of dry hydrochloric-acid gas. It is a colorless mass, which deliquesces in the air, is volatile at a high temperature ; and determinations of the specific gravity of its vapor made at very high temperatures have shown that its molecule under these conditions should be represented by the formula $FeCl_2$. At lower temperatures the molecule appears to be more complex. The evidence on this point is not conclusive. If allowed to stand in contact with the air in hydrochloric-acid solution, it is changed to ferric chloride :

$$2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O.$$

If hydrochloric acid is not present, a basic chloride is precipitated and ferric chloride is then in the solution :

$$4FeCl_2 + H_2O + O = 2Fe{<}{}^{OH}_{Cl} + 2FeCl_3.$$

When treated with oxidizing agents in general, as nitric

acid, potassium chlorate, potassium permanganate, etc., it is converted into ferric chloride.

Ferrous chloride, like most other metallic chlorides, combines with the chlorides of the strongest basic elements, forming double compounds. Those with potassium and sodium chlorides have the formulas $FeCl_2.2KCl$ or $K_2FeCl_4$, and $FeCl_2.2NaCl$ or $Na_2FeCl_4$. It combines also with other chlorides, such as those of mercury and cadmium, forming similar salts.

A solution of ferrous chloride made by dissolving iron in hydrochloric acid is used in medicine under the name *Liquor Ferri chlorati*. It contains ten per cent iron.

**Ferric Chloride, $FeCl_3$.**—As stated in the last paragraph, ferrous chloride is readily converted into ferric chloride by oxidation. The simplest way to make a solution of the ferric compound is to dissolve iron in hydrochloric acid and pass chlorine into it to complete saturation. The solution is decomposed by heating, especially if dilute, yielding hydrochloric acid and an insoluble oxychloride. The chloride can be obtained in yellow crystals with six or twelve molecules of water. Like the ferrous compound, it is decomposed into hydrochloric acid and the oxide when heated. Anhydrous ferric chloride is obtained by heating iron wire in dry chlorine. It forms black, lustrous crystalline laminæ, is volatile at a lower temperature than the ferrous compound, and the specific gravity of the vapor is that required by a compound whose molecule corresponds to the formula $FeCl_3$. When treated with nascent hydrogen, ferric chloride is converted into ferrous chloride:

$$FeCl_3 + H \doteq FeCl_2 + HCl.$$

It combines with other chlorides, forming double chlorides. A solution of ferric chloride is used in medicine under the name *Liquor Ferri sesquichlorati*.

**Cyanides.**—The compounds which iron forms with cyanogen are of special interest. The simple compounds, ferrous cyanide, $Fe(CN)_2$, and ferric cyanide, $Fe(CN)_3$, corresponding to the above-mentioned chlorides, are not known: only double compounds of these with

other cyanides are well known, and some of them are manufactured on the large scale. When a solution of potassium cyanide acts upon metallic iron or the oxides of iron, a solution is formed from which the salt known as *potassium ferrocyanide* or *yellow prussiate of potash* crystallizes. This has the composition $K_4Fe(CN)_6 + 3H_2O$, and may be regarded as made up of a molecule of ferrous cyanide and four molecules of potassium cyanide, as represented in the formula $Fe(CN)_2.4KCN + 3H_2O$. When this salt is treated with chlorine it is converted into *potassium ferricyanide*, or *red prussiate of potash*, $K_3Fe(CN)_6$, which is to be regarded as consisting of ferric cyanide and potassium cyanide, as represented in the formula $Fe(CN)_3.3KCN$. The transformation is represented thus:

$$K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl.$$

From these two a number of other cyanogen compounds are obtained. When treated in concentrated solution with concentrated hydrochloric acid they yield the free acids, and by treating them with solutions of different metallic salts corresponding salts of these acids are obtained. Among the most important of these derivatives are the following:

Ferrohydrocyanic acid,
     $H_4Fe(CN)_6$
Potassium ferrocyanide,
     $K_4Fe(CN)_6$
Sodium ferrocyanide,
     $Na_4Fe(CN)_6$
Barium ferrocyanide,
     $Ba_2Fe(CN)_6$
Ferric ferrocyanide,
     $Fe_4[Fe(CN)_6]_3$
Ferri-potassium ferrocyanide,
     $KFeFe(CN)_6$

Ferrihydrocyanic acid,
     $H_3Fe(CN)_6$
Potassium ferricyanide,
     $K_3Fe(CN)_6$
Sodium ferricyanide,
     $Na_3Fe(CN)_6$

Ferrous ferricyanide,
     $Fe_3[Fe(CN)_6]_2$

**Potassium Ferrocyanide, $K_4Fe(CN)_6 + 3H_2O$.**—As stated above, this salt can be made by treating iron or the oxides of iron with a solution of potassium cyanide. On the large scale it is manufactured by melting crude potash or potassium carbonate, and gradually adding a mixture of iron filings or turnings, and refuse animal-

matter, as claws, horns, hoofs, hair, etc. Or the potash is melted with the animal substances and potassium cyanide thus formed, and this treated in solution with ferrous carbonate, when the ferrocyanide is formed. It forms large yellow pyramids belonging to the tetragonal system. At the ordinary temperature it dissolves in three to four parts of water, and more easily in hot water. It gives up its water of crystallization very easily. When heated it is decomposed, forming potassium cyanide, nitrogen, and a compound of iron and carbon:

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2.$$

Treated with concentrated sulphuric acid it undergoes decomposition, giving as gaseous product carbon monoxide, and this furnishes a good method for the preparation of the gas:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 \\ + 3(NH_4)_2SO_4 + 6CO.$$

With dilute sulphuric acid it gives hydrocyanic acid, and forms at the same time a white insoluble compound of the composition $KFe(CN)_3$ or $Fe(CN)_2.KCN$:

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + 3K_2SO_4 + 2KFe(CN)_3.$$

**Ferrohydrocyanic Acid, $H_4Fe(CN)_6$,** formed as above described, is a white crystalline substance, which is easily soluble in water and alcohol. It takes up oxygen from the air, and is converted into the ferric salt of the acid, hydrocyanic acid being given off. The ferric salt is the substance commonly called *insoluble Prussian blue.* The relation of the salt to the acid is shown by the formulas

<div align="center">

$H_4Fe(CN)_6$         $Fe_4[Fe(CN)_6]_3$

Ferro-hydrocyanic acid     Ferric ferrocyanide, or
Prussian blue

</div>

**Ferric Ferrocyanide, or Prussian Blue, $Fe_4[Fe(CN)_6]_3$.**— This compound is very readily formed by adding a solution of a ferric salt to a solution of potassium ferrocyanide, and appears as a dark-blue precipitate:

$$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

It is obtained in pure condition by treating a solution of a ferric salt with a solution of ferrohydrocyanic acid. When a ferric salt is added to an excess of potassium ferrocyanide a ferri-potassium salt, $KFeFe(CN)_6$, is formed. This is commonly called Prussian blue, and the commercial article always contains some of it. It is also known as soluble Prussian blue. When heated with an alkaline hydroxide, Prussian blue is decomposed, the products of the action being the ferrocyanides of the alkali metals and ferric hydroxide:

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3.$$

**Potassium Ferricyanide, $K_3Fe(CN)_6$.** — This salt is formed by treating the ferrocyanide, either dry or in solution, with chlorine. It forms large, dark-red, monoclinic prisms. It dissolves in about three times its weight of water at the ordinary temperature, and is more easily soluble in hot water. In alkaline solution it acts as a strong oxidizing agent, on account of its tendency to form the ferrocyanide. The character of the action is indicated by the following equation:

$$6K_3Fe(CN)_6 + 6KOH = 6K_4Fe(CN)_6 + 3H_2O + 3O.$$

**Ferrihydrocyanic Acid, $H_3Fe(CN)_6$,** is a crystallized substance.

**Ferrous Ferricyanide, $Fe_3[Fe(CN)_6]_2$,** is commonly called Turnbull's blue. It is formed by adding potassium ferricyanide to a solution of ferrous sulphate, or any ferrous salt:

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4.$$

Starting with ferrocyanic and ferricyanic acids, four iron salts suggest themselves. These are ferrous and ferric ferrocyanide, and ferrous and ferric ferricyanide. The relations between them are indicated in the following formulas:

|  |  |  |  |
|---|---|---|---|
| Acid, . . . . . $H_4Fe(CN)_6$ | | Acid, . . . . $H_3Fe(CN)_6$ | |
| (1) Ferrous salt, . $Fe_2Fe(CN)_6$ | | (3) Ferrous salt, . $Fe_3[Fe(CN)_6]_2$ | |
| (2) Ferric salt, . . $Fe_4[Fe(CN)_6]_3$ | | (4) Ferric salt, . . $FeFe(CN)_6$ | |

Of these (2) is Prussian blue and (3) is Turnbull's blue. The commercial Prussian blue contains some Turnbull's blue. The reason of this appears to be that a part of the ferrocyanide of potassium used in the preparation is oxidized by the ferric salt, and thus ferricyanide of potassium and a ferrous salt come together. When potassium ferrocyanide is added to a solution of a ferrous salt, we should expect the formation of salt (1) or ferrous ferrocyanide:

$$K_4Fe(CN)_6 + 2FeCl_2 = Fe_2Fe(CN)_6 + 4KCl.$$

But instead of this a ferro-potassium salt, of the formula $K_2FeFe(CN)_6$, is formed:

$$K_4Fe(CN)_6 + FeCl_2 = K_2FeFe(CN)_6 + 2KCl.$$

This is a white powder, which is formed also when potassium ferrocyanide is decomposed by dilute sulphuric acid in the preparation of hydrocyanic acid. It is represented above by the formula $KFe(CN)_3$, but taking the method of formation into consideration the formula $K_2FeFe(CN)_6$ seems more probable. Ferric ferricyanide is not known. When, however, a solution of a ferric salt is added to one of potassium ferricyanide the solution turns dark brown, and perhaps contains this salt. The composition of the salt is the same as that of ferric cyanide, and possibly the two compounds are identical.

**Nitroprussiates.**—When potassium ferrocyanide is treated with nitric acid, potassium nitrate is formed. When this is removed and the solution neutralized with sodium carbonate, a salt known as sodium nitroprussiate is obtained. This crystallizes very beautifully, and is used to some extent in the laboratory. With soluble sulphides it gives an intense violet color, but not with hydrogen sulphide. The composition of the salt is represented by the formula $Na_2Fe(CN)_5(NO) + 2H_2O$. The free acid corresponding to this salt, and also other salts of the same acid, have been made.

**Ferrous Hydroxide, Fe(OH)₂**, is formed when a soluble hydroxide is added to a solution of a ferrous salt. It is a white precipitate, but it is usually obtained as a greenish mass, as it is very easily oxidized by the oxygen of

the air and that contained in the solutions. When allowed to stand in contact with the air it turns a dirty green, and finally brown, being converted into ferric hydroxide. When heated in the air it loses water, and takes up oxygen, forming ferric oxide.

**Ferrous Oxide, FeO,** is formed by passing hydrogen over ferric oxide heated to 300°. It is a black powder, which takes up oxygen from the air, and is converted into the oxide $Fe_2O_3$.

**Ferric Hydroxide, Fe(OH)₃.**—This compound is formed most readily by adding ammonia to a solution of a ferric salt, when it appears as a voluminous brownish-red precipitate. When filtered, washed, and dried, its composition is not changed. If heated at 100°, or if the solution is boiled for some time, it loses water, and forms compounds of the formulas $FeO.OH$, $Fe_2O(OH)_4$, etc. The latter is derived from the normal hydroxide as represented in the equation

$$2Fe(OH)_3 = Fe_2O(OH)_4 + H_2O.$$

The mineral pyrosiderite is the hydroxide $FeO.OH$. Brown iron ore is $Fe_4O_3(OH)_6$; and bog iron-ore is $Fe_2O(OH)_4$. All of these are derivatives of the normal hydroxide. The normal hydroxide differs from aluminium hydroxide in the fact that it has no acid properties. Therefore, if the two hydroxides are treated together with a caustic alkali only the aluminium hydroxide dissolves. The compound $FeO.OH$, corresponding to $AlO.OH$ and $CrO.OH$, yields salts under some circumstances. Thus a calcium salt, $\dfrac{FeO.O}{FeO.O}{>}Ca$, is formed by heating together ferric oxide and lime to a high temperature. In composition this is plainly analogous to the spinels. Magnetic oxide of iron or magnetite is believed to be the corresponding ferrous salt, $\dfrac{FeO.O}{FeO.O}{>}Fe$. Franklinite also is a salt of the same order, containing zinc. It is essentially a zinc salt, of the formula $\dfrac{FeO.O}{FeO.O}{>}Zn$, but some of the zinc is replaced by iron and manganese.

**Ferrous-Ferric Oxide, $Fe_3O_4$.**—As stated above, this compound is regarded as analogous to the spinels, and as the ferrous salt of the acidic hydroxide $FeO.OH$, as represented in the equation $(FeO.O)_2Fe$. It is found in nature as the mineral magnetite, and loadstone, which occurs in Sweden, Norway, and elsewhere. It is, further, formed when iron is burned in oxygen, and when water is passed over red-hot iron. Some of the magnetite which occurs in nature has the power to attract iron, or is magnetic.

**Soluble Ferric Hydroxide** is formed when a solution of ferric chloride or ferric acetate is treated with ferric hydroxide, and the solution thus formed dialyzed (see page 421). The ferric salts pass through the membrane, and the ferric hydroxide remains in solution in water, forming a deep-red liquid. It is used in medicine. Small quantities of salts cause the precipitation of ferric hydroxide from the solution.

**Ferric Oxide, $Fe_2O_3$,** is found in nature, and is known as hematite, forming one of the most valuable ores of iron. It can be made in the laboratory by igniting the hydroxide. As hematite, it is a black, crystallized substance with a high lustre. Otherwise it has a red or a reddish-brown color. The oxide found in nature and that which has been strongly ignited are very difficultly soluble in acids. In the preparation of fuming sulphuric acid by heating ferrous sulphate (see page 219) there is left a residue of ferric oxide known as *rouge*, which is used as a red pigment and as a polishing powder. A specially fine variety of rouge for polishing is manufactured by heating ferrous oxalate, $FeC_2O_4$, in contact with the air.

**Ferrous Sulphide, FeS,** is formed by direct union of iron and sulphur when the two are heated together. It is manufactured by heating iron filings and sulphur together in a crucible. The pure compound is yellow and crystalline. When heated in contact with the air it is oxidized to ferrous sulphate, if the temperature is not too high. At a higher temperature the products are sulphur dioxide and ferric oxide. When a solution of a

ferrous salt is treated with ammonium sulphide, ferrous sulphide is precipitated as a black powder. When a ferric salt is treated with ammonium sulphide it is reduced to the ferrous condition, and then ferrous sulphide is precipitated :

$$Fe_2(SO_4)_3 + (NH_4)_2S = 2FeSO_4 + (NH_4)_2SO_4 + S ;$$
$$2FeSO_4 + 2(NH_4)_2S = 2FeS + 2(NH_4)_2SO_4.$$

The sulphide thus obtained oxidizes readily in the air, and forms the sulphate. The compact variety is used in making hydrogen sulphide (which see).

**Ferric Sulphide, $Fe_2S_3$,** is analogous to ferric oxide, $Fe_2O_3$. It is formed artificially by heating iron and sulphur together in the proper proportions.

Just as there are salts derived from the hydroxide FeO.OH, so there are salts which are derived from the corresponding sulphide FeS.SH. The potassium, sodium, and some other salts are obtained artificially. Chalcopyrite is apparently the cuprous salt SFe–S–Cu or $FeCuS_2$.

**Ferrous Carbonate, $FeCO_3$.**—This salt occurs in nature as spathic iron or siderite. It crystallizes in forms similar to those of calc spar or calcium carbonate $CaCO_3$. Like this, further, it dissolves in water which contains carbon dioxide, and is therefore contained in natural waters which come in contact with it. When a solution of a ferrous salt is treated with a soluble carbonate a white precipitate is formed, which is ferrous carbonate ; but in contact with the air this is rapidly oxidized and decomposed, leaving ferric hydroxide, which with carbonic acid does not form a salt. In this respect ferric hydroxide acts like aluminic and chromic hydroxides, and therefore when a soluble carbonate is added to a solution of a ferric salt the hydroxide and not ferric carbonate is thrown down.

**Ferrous Sulphate, $FeSO_4$.**—This important compound is manufactured on the large scale by the spontaneous oxidation of pyrite in contact with the air, and by dissolving iron in sulphuric acid. It is frequently called

"green vitriol" (see p. 596), and more commonly " copperas." Under ordinary conditions it crystallizes in transparent, green, monoclinic crystals with seven molecules of water, just as zinc sulphate, magnesium sulphate, etc., do; and when heated, six of these are given off readily, while the last is given off with difficulty—a fact which makes it appear probable that the salt is a derivative of tetrahydroxyl-sulphuric acid, as represented in

the formula $OS\left\{\begin{array}{l}(OH)_2 \\ O \\ O\end{array}\right. > Fe$. While it ordinarily crystal-

lizes in monoclinic crystals, it takes the rhombic form if its supersaturated solution is touched with a crystal of zinc sulphate. It also crystallizes in the triclinic system with five molecules of water, like cupric sulphate, if a crystal of the latter salt is placed in its concentrated solution. The salt undergoes change when exposed to the air, being converted into a compound containing ferric sulphate, $Fe_2(SO_4)_3$, and ferric hydroxide, or more probably a basic ferric sulphate, $Fe_3(SO_4)_3(OH)_3$.

$$6FeSO_4 + 3O + 3H_2O = 2Fe_3(SO_4)_3(OH)_3, \text{ or}$$
$$6FeSO_4 + 3O + 3H_2O = 2Fe_2(SO_4)_3 + 2Fe(OH)_3.$$

The same change takes place when a solution of ferrous sulphate is exposed to the air. When treated with oxidizing agents in the presence of sulphuric acid it is completely converted into ferric sulphate:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Like other soluble ferrous salts it absorbs nitric oxide, and when the solution of the unstable compound is heated the nitric oxide is given off. Ferrous sulphate is used in dyeing, in the manufacture of ink, etc.; and as a deodorizer. With sulphates of the alkalies ferrous sulphate forms double salts, such as $FeK_2(SO_4)_2 + 6H_2O$, $Fe(NH_4)_2(SO_4)_2 + 6H_2O$, etc. These are not as easily oxidized as the simple salt, and are convenient in the laboratory when a pure ferrous salt is wanted. It is a fact worthy of special notice, that while ferrous sulphate crystallizes

with seven molecules of water, these salts contain only six molecules, and all of this is easily given off when the salts are heated. It appears, therefore, that these double salts are formed from ferrous sulphate by replacing one molecule of the water by a molecule of some sulphate. This is clear if ferrous sulphate and the other salts are regarded as salts of tetrahydroxyl-sulphuric acid. We should then have the relation between the double sulphate and the simple ones as represented in the formulas below:

$$Fe{<}{O \atop O}{>}S{<}{O \atop O}\Big|{H \atop H}\qquad {HO \atop HO}\Big|{O \atop}{>}S{<}{OK \atop OK}$$

Ferrous sulphate          Potassium sulphate

$$Fe{<}{O \atop O}{>}S{<}{O \atop O}{>}S{<}{OK \atop OK} = FeK_2(SO_4)_2$$

Ferrous-potassium sulphate

**Ferric Sulphate, $Fe_2(SO_4)_3$.**—This salt, as stated in the last paragraph, is formed by oxidation of ferrous sulphate. It is also formed by dissolving ferric oxide or hydroxide in sulphuric acid. When the solution is evaporated the salt remains behind as a white, anhydrous mass. It readily forms basic salts, the composition of which is not positively known. With the sulphates of the alkali metals it forms double salts, which are perfectly analogous to alum, and are known as the iron alums; as, for example, $FeK(SO_4)_2 + 12H_2O$, $Fe(NH_4)(SO_4)_2 + 12H_2O$, etc.

**Ferrous Phosphate, $Fe_3(PO_4)_2$,** occurs in nature crystallized with eight molecules of water as the mineral vivianite. Both this salt and ferric phosphate, $FePO_4$, are insoluble and are formed when solutions of ferrous and ferric salts are treated with sodium phosphate.

**Ferric Acid, $H_2FeO_4$,** is analogous in composition to chromic and manganic acids. The acid itself is not known, but its potassium salt is formed when iron or ferric oxide is heated with saltpeter, or when chlorine is passed into

caustic potash containing ferric hydroxide in suspension:

$$Fe(OH)_3 + 2KOH + 3Cl = K_2FeO_4 + H_2O + 3HCl.$$

This, as well as the other ferrates, is unstable, the iron tending to pass back into the condition of a ferric compound.

**Iron Disulphide, FeS₂,** is not analogous to any oxygen compound of iron. In it the metal appears to be quadrivalent. The disulphide occurs very widely distributed and in large quantities in nature as the mineral iron pyrites or pyrite, which crystallizes in the regular system, and as marcasite, which crystallizes in the rhombic system. It can be made artificially, and if crystallized it appears in the form of pyrite. Its conduct under the influence of heat has been repeatedly referred to in connection with the roasting of iron and other ores. As pyrite it has a golden-yellow color, and it has frequently been taken for the precious metal by those not familiar with it. The name "fool's gold," by which it is sometimes popularly known, suggests this fact.

*Arsenopyrite*, FeAsS, occurs in nature, and is a valuable source of the element arsenic; for, as has been stated (see p. 305), when it is heated it gives off arsenic, and ferrous sulphide is left behind.

**Iron Carbonyls.**—When finely-divided iron is allowed to cool in hydrogen gas to 80°, and then treated with carbon monoxide, the issuing gas imparts a yellow color to the flame of a Bunsen burner, and by passing it through a heated glass tube a metallic mirror is formed at between 200° and 350°. This mirror consists of iron. These phenomena are due to the formation of volatile compounds of iron with carbon monoxide, the principal one having the composition $Fe(CO)_5$. (See Nickel Carbonyl.)

**Reactions which are of Special Value in Chemical Analysis.**—*Ferrous Compounds.*— The reactions of ferrous compounds with the *soluble hydroxides* and *carbonates, ammonium sulphide, potassium ferricyanide*, and with *oxidizing agents* have been explained above. With ammonium salts ferrous chloride forms double salts, which are soluble; therefore, if ammonium chloride is added to a

solution of the salt ammonia does not precipitate the hydroxide. Further, ammonia does not completely precipitate the hydroxide from a solution of a ferrous salt, as an ammonium salt is formed. By standing in the air, however, these solutions containing the double salts are oxidized, and ferric hydroxide is precipitated. The reactions with potassium cyanide will be understood from what has been said concerning the compounds of ferrohydrocyanic and ferrihydrocyanic acids.

*Ferric Compounds.*—The reactions of ferric compounds with the *soluble hydroxides* and *carbonates, ammonium sulphide, potassium ferrocyanide,* and *potassium ferricyanide* have been explained above. When *hydrogen sulphide* is passed through a solution of a ferric salt, reduction to the corresponding ferrous salt takes place, and sulphur separates, which gives the solution a milky appearance:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S ;$$
$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

When a neutral solution of a ferric salt is treated with *suspended barium carbonate* the iron is precipitated as the hydroxide.

When a neutral solution of a ferric salt is treated with *acetate of potassium* or *sodium* it turns dark red, in consequence of the formation of ferric acetate which remains in solution. When the solution is boiled the acetate breaks down into acetic acid and ferric hydroxide, which is precipitated:

$$FeCl_3 + 3NaC_2H_3O_2 = Fe(C_2H_3O_2)_3 + 3NaCl ;$$
$$Fe(C_2H_3O_2)_3 + 3H_2O = Fe(OH)_3 + 3C_2H_4O_2.$$

When *potassium sulphocyanate,* KCNS, is added to a solution of a ferric salt a blood-red color is produced. This occurs even in extremely dilute solutions of ferric salts.

The borax bead is colored bottle-green in the reducing flame, and brown-red to yellowish red in the oxidizing flame, when treated with compounds of iron.

COBALT, Co (At. Wt. 58.49).

**General.**—As stated in the remarks introductory to the iron group, cobalt, like nickel, preferably forms compounds which are analogous to ferrous compounds. It, however, forms a few which are analogous to ferric compounds, its power in this direction being greater than that of nickel. Its salts form a great variety of compounds with ammonia, and these have been extensively studied.

**Occurrence and Preparation.**—Cobalt occurs in nature, almost always in company with nickel. The principal minerals containing it are smaltite, $CoAs_2$, and cobaltite, $CoS_2.CoAs_2$. In each of these a part of the cobalt is replaced by iron, and, generally, some nickel. By roasting and melting the ores in blast-furnaces they are partly purified. The product is dissolved in hydrochloric acid, and treated with a small quantity of calcium hypochlorite and hydroxide for the purpose of removing iron and arsenic; then with hydrogen sulphide to remove copper and bismuth; and finally with calcium hypochlorite when cobaltic hydroxide, $Co(OH)_3$, is precipitated. This is readily converted into the oxide, $Co_2O_3$, from which the metal can be prepared by heating it in a current of hydrogen. It is also obtained by heating the oxalate to a sufficiently high temperature.

**Properties.**—Cobalt has a silver-white color, with a slight cast of red. It is harder than iron, and melts at a somewhat lower temperature; is tenacious; and has the specific gravity 8.9. It dissolves in nitric acid.

**Cobaltous Chloride,** $CoCl_2$, is formed by heating cobalt in chlorine gas, and in solution by treating cobalt carbonate with hydrochloric acid. From the solution it crystallizes in dark-red prisms of the composition $CoCl_2 + 6H_2O$. The anhydrous salt is blue. When the blue salt is treated with water it turns red, and when the red salt is heated it turns blue. This difference in color between the anhydrous and the hydrated salts is characteristic of cobalt salts. If marks are made on paper with a dilute solution of one of the salts the color is not perceptible. If, however, the paper is held before a fire, the salt loses water and turns blue, and as the blue

is more intense than the red, it is visible. When the salt becomes moist again it becomes invisible. This is the basis for the preparation of the so-called *sympathetic inks*.

**Cobaltous Hydroxide, Co(OH)₂**, is formed as a red precipitate when a soluble hydroxide is added to a cobaltous salt, and the blue precipitate, which is first formed and which is a basic salt, is allowed to stand. It is oxidized by contact with the air, forming cobaltic hydroxide, which breaks down into *cobaltic oxide*, $Co_2O_3$.

**Cobaltous Oxide, CoO**, is formed when the corresponding hydroxide is carefully heated without access of air. When heated in the air it is converted into *cobaltous-cobaltic oxide*, $Co_3O_4$, which is analogous to ferrous-ferric oxide. This is also formed when cobaltic oxide, $Co_2O_3$, is heated in the air.

**Cobaltic Hydroxide, Co(OH)₃**, is formed when calcium hypochlorite is added to a solution of a cobaltous salt, and is a black powder. When heated it is converted into black *cobaltic oxide*, $Co_2O_3$.

**Cobalt Sulphide, CoS**, is the black precipitate which is formed by adding ammonium sulphide to a cobaltous salt. It is not soluble in dilute acids, and differs from ferrous sulphide in this respect. Other sulphides of cobalt are those of the formulas $Co_3S_4$ and $CoS_2$. The former is found in nature, and is known as linnæite. The latter occurs in combination with other sulphides, as in cobaltite, $CoS_2.CoAs_2$.

**Cyanides.**—Cobaltous cyanide is an insoluble dirty-red compound which is formed when potassium cyanide is added to a solution of a cobalt salt. It dissolves in an excess of potassium cyanide, forming a double cyanide, $K_4Co(CN)_6$, which is analogous to potassium ferrocyanide. When this solution is boiled the cyanide is oxidized, forming a compound analogous to potassium ferricyanide, thus:

$$2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KOH.$$

This acts like the corresponding iron compound. The cobalt is not precipitated from it by ammonium sulphide

or sodium hydroxide. This conduct towards potassium cyanide distinguishes cobalt from nickel salts.

**Smalt.**—The beautiful pigment known by this name is essentially a cobalt glass in which cobalt takes the place of calcium. It is made by heating compounds of cobalt with quartz and potassium carbonate. The glass thus formed is powdered very finely and used as a pigment. It does not change color in the sunlight, and is not affected by acids nor by alkalies.

**Compounds of Ammonia with Salts of Cobalt.**—In general, when solutions of cobalt salts in ammonia are exposed to the air they undergo oxidation, and complicated salts are formed. In the case of cobaltous chloride, the first product formed is one of the composition $Co(NH_3)_2Cl_2 + H_2O$, which is known as *dichro-cobaltic chloride*. At the same time another compound of the composition $Co(NH_3)_4Cl_3 + H_2O$, known as *praseo-cobaltic chloride*, is formed. If a solution of cobaltous chloride in concentrated ammonia is allowed to stand longer than is required to form the preceding compound, or if an oxidizing agent is used, the product has the composition $Co(NH_3)_5Cl_3$, and is known as *purpureo-cobaltic chloride*. And, finally, by further action of oxidizing agents, *luteo-cobaltic chloride*, $Co(NH_3)_6Cl_3$, is formed. It will be observed that these compounds form a series, the members of which differ from one another by $NH_3$ or a multiple:

$$Co(NH_3)_2Cl_3 ; \quad Co(NH_3)_4Cl_3 ; \quad Co(NH_3)_5Cl_3 ; \quad Co(NH_3)_6Cl_3.$$

They may be regarded as made up of cobaltic chloride and different numbers of molecules of ammonia. In regard to the first one, it is simplest to consider it as analogous to the mercur-ammonium compounds (see page 633). Accordingly, it is usually represented as derived from three molecules of ammonium chloride by the substitution of a trivalent atom of cobalt for three hydrogen atoms.

When a solution of cobaltous chloride in ammonia, which has become red by contact with the air, is treated at the ordinary temperature with concentrated hydrochloric acid, a brick-red precipitate of *roseo-cobaltic chlo-*

*ride*, which has the same composition as purpureo-cobaltic chloride, $Co(NH_3)_5Cl_3$, with a molecule of water, is formed.

If in the above reactions the nitrate or sulphate of cobalt is used, nitrates and sulphates corresponding to the chlorides mentioned are obtained.

Thus:

| *Roseo-salts.* | *Luteo-salts.* |
|---|---|
| $Co(NH_3)_5Cl_3$ | $Co(NH_3)_6Cl_3$ |
| $Co(NH_3)_5(NO_3)_3$ | $Co(NH_3)_6(NO_3)_3$ |
| $[Co(NH_3)_5]_2(SO_4)_3$ | $[Co(NH_3)_6]_2(SO_4)_3$ |

## NICKEL, Ni (At. Wt. 58.24).

**General.**—Nickel differs from cobalt in respect to the difficulty with which it forms nickelic compounds or those in which it is trivalent. At the same time it does form an oxide of the composition $Ni_2O_3$, and the corresponding hydroxide, $Ni(OH)_3$. In all other compounds it is bivalent, the compounds being analogous to ferrous compounds.

**Occurrence and Preparation.**—Nickel occurs native in meteorites. The principal minerals containing it are the arsenide, NiAs, known as niccolite, and the sulpharsenide, NiSAs or $NiS_2.NiAs_2$, known as gersdorffite. From the ores the oxide is obtained in the same way that cobalt oxide is obtained from its ores. This is then pressed in the form of small cubes, mixed with charcoal powder, and ignited. The commercial metal is generally found in the form of these cubes.

**Properties.**—Nickel is a white metal with a slight cast of yellow. It is very hard, and capable of a high polish. The metal in its ordinary condition is brittle, but after treatment with a little magnesium it becomes very malleable. Its specific gravity is 8.9, and it melts at a high temperature. It is not changed in the air; it dissolves slowly in hydrochloric and sulphuric acids, and readily in nitric acid. Like iron, it is magnetic.

**Alloys.**—Alloys of nickel are extensively used. *Argentan* or *German silver* consists of copper, zinc, and nickel. Various nickel alloys are used for making coins. The 5 and 3 cent pieces in the United States are made of an

alloy consisting of 25 per cent nickel and 75 per cent copper. In Switzerland, and Belgium also, nickel coins are used.

**Other Applications of Nickel.**—Besides as a constituent of important alloys, nickel is extensively used at present in nickel-plating. Iron objects are covered with a thin layer of the metal for the purpose of protecting them from rusting. The plating is accomplished as silver-plating and copper-plating are—by means of electrolysis, a bath of nickel-ammonium sulphate being used.

**Nickelous Chloride, $NiCl_2$,** crystallizes from aqueous solution with six molecules of water, and the crystals are green. When the water of crystallization is driven off they become yellow. In general, nickel salts, with their water of crystallization, are green, and in the anhydrous condition they are yellow.

**Nickelous Hydroxide, $Ni(OH)_2$,** is formed when a nickel salt is treated with a soluble hydroxide, and is a green insoluble substance. When heated it is converted into the green *oxide*, NiO.

**Nickelic Hydroxide, $Ni(OH)_3$,** is precipitated as a black powder when a solution of a nickel salt is treated with sodium hypochlorite.

**Cyanides.**—When potassium cyanide is added to a solution of a nickel salt, nickel cyanide, $Ni(CN)_2$, is precipitated as a greenish-white substance. With an excess of potassium cyanide this forms the salt, $Ni(CN)_2.2KCN$, which, owing to the fact that nickelous salts are not converted into nickelic salts by oxidation, does not undergo change when boiled with potassium cyanide. When hydrochloric acid is added to a solution of the double cyanide, nickelous cyanide is precipitated. If boiled with precipitated mercuric oxide the double cyanide is decomposed and nickel oxide is thrown down.

**Nickel Carbonyl, $Ni(CO)_4$.**—This interesting compound is formed when finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400°, is allowed to cool in a slow current of carbon monoxide. A gas is formed which can easily be condensed, its boiling-point being 43°. At $-25°$ it solidifies forming

needle-shaped crystals. When the gas is passed through a heated tube pure nickel is deposited. Advantage of this fact is taken for the purpose of preparing pure nickel on the large scale. Cobalt does not form a compound of this kind.

**Reactions of Cobalt and Nickel which are of Special Value in Chemical Analysis.**—The reactions with the *soluble hydroxides* have been explained. With *ammonium sulphide* both give black sulphides, which are not easily dissolved by dilute hydrochloric acid. From solutions of the acetates *hydrogen sulphide* precipitates the sulphides. Nickel sulphide is slightly soluble in ammonium sulphide, and the solution has a brownish-yellow color.

The action of the hypochlorites upon solutions of nickel and cobalt salts has been explained above. The reactions with potassium cyanide have also been explained. These furnish a good method for separating the two metals.

When a solution of *potassium nitrite* is added to a solution of a cobalt salt containing free acetic acid or nitric acid, a precipitate of cobaltic potassium nitrite is formed. This is a compound of cobaltic nitrite, $Co(NO_2)_3$, and potassium nitrite, of the composition $Co(NO_2)_3.3KNO_2$. The formation involves oxidation of the cobaltous salt, and this is effected by some of the nitrogen trioxide which is set free. Thus with the chloride the action may be represented as follows:

$$CoCl_2 + 7KNO_2 + 2C_2H_4O_2 =$$
$$2KCl + Co(NO_2)_3.3KNO_2 + 2KC_2H_3O_2 + H_2O + NO.$$

Nickel does not form a similar compound of a nickelic salt, but simply forms a double nitrite, containing the nickelous salt $Ni(NO_2)_2.4KNO_2$.

Cobalt compounds color the bead of microcosmic salt blue both in the reducing and oxidizing flame. Nickel colors it reddish brown in the oxidizing flame when hot, and pale yellow when cold. In the reducing flame it is gray.

# CHAPTER XXXIV.

### ELEMENTS OF FAMILY VIII, SUB-GROUP B : RUTHENIUM—RHODIUM—PALLADIUM.

### ELEMENTS OF FAMILY VIII, SUB-GROUP C : OSMIUM—IRIDIUM—PLATINUM.

**General.**—Comparing the members of the three sub-groups of Family VIII, with reference to their atomic weights and specific gravities, we have the following remarkable table :

| Fe | Co | Ni |
|---|---|---|
| At. Wt.  55.6 | At. Wt.  58.49 | At. Wt.  58.24 |
| Sp. Gr.  7.8 | Sp. Gr.  8.5 | Sp. Gr.  8.8 |

| Ru | Rh | Pd |
|---|---|---|
| At. Wt. 100.91 | At. Wt. 102.23 | At. Wt. 105.56 |
| Sp. Gr.  12.26 | Sp. Gr.  12.1 | Sp. Gr.  11.5 |

| Os | Ir | Pt |
|---|---|---|
| At. Wt. 189.55 | At. Wt. 191.66 | At. Wt. 193.41 |
| Sp. Gr.  22.48 | Sp. Gr.  22.42 | Sp. Gr.  21.50 |

It will be observed that the atomic weights and specific gravities of the members of each sub-group are approximately the same. But just as there is a gradual change in the chemical conduct as we pass from iron to nickel in the iron group, so a similar gradation of properties is observed in the other two groups. As far as the variety of compounds which they form is concerned, ruthenium and osmium are more like iron than they are like rhodium and iridium. Further, rhodium and iridium resemble each other, as regards the variety of their compounds, more closely than they resemble palladium and platinum, and a similar resemblance is noticed between palladium and platinum. These relations will appear

(719)

more clearly if the formulas of some of the principal compounds of the elements under consideration are placed together in a table.

| Ru and Os | | Rh and Ir | | Pd and Pt | |
|---|---|---|---|---|---|
| $RuO_4$ | $OsO_4$ | $RhO_2$ | $IrO_2$ | $PdO_2$ | $PtO_2$ |
| $HRuO_4$ | | $Rh_2O_3$ | $Ir_2O_3$ | $PdO$ | $PtO$ |
| $H_2RuO_4$ | $H_2OsO_4$ | $RhO$ | $IrO$ | $Pd_2O$ | |
| $RuO_2$ | $OsO_3$ | | $IrCl_4$ | $PdCl_4$ | $PtCl_4$ |
| $Ru_2O_3$ | $Os_2O_3$ | $RhCl_3$ | $IrCl_3$ | $PdCl_2$ | $PtCl_2$ |
| $RuO$ | $OsO$ | | $IrCl_2$ | | |
| $RuCl_4$ | $OsCl_4$ | | | | |
| $RuCl_3$ | $OsCl_3$ | | | | |
| $RuCl_2$ | $OsCl_2$ | | | | |

The elements ruthenium and osmium have a more acidic character than the others; just as iron has a more acidic character than cobalt and nickel. Ruthenium forms not only ruthenious acid, $H_2RuO_4$, which is analogous to ferric, chromic, and manganic acids, but also perruthenious acid analogous to permanganic acid. Osmium forms osmious acid, $H_2OsO_4$, but apparently no perosmious acid. The highest known oxides are derived from these elements. These are the tetroxides, $RuO_4$ and $OsO_4$, in which the elements appear to be octovalent. Neither rhodium nor iridium forms acids. As far as their oxides and chlorides are concerned, they suggest manganese more than any other element, but their oxides have only weak basic properties. Passing finally to the last pair, palladium and platinum, we find that they have not the power to form oxides of the general formula $M_2O_3$, but that they act as the members of Family IV do—either as bivalent or quadrivalent elements. Palladium, to be sure, forms a compound, the sub-oxide $Pd_2O$, which is like the oxide of silver, $Ag_2O$, and in which it appears to be univalent. In fact the members of Family VIII form the connecting link between the members of Family VII and those of Family I. In manganese, as we have seen, a maximum of power is reached as far as the valence is concerned. It forms compounds in which it appears to

be septivalent, sexivalent, quadrivalent, trivalent, and bivalent. When we pass to iron, however, we find that it is not septivalent. In its most complex compounds this element is sexivalent, as in ferric acid, $H_2FeO_4$, but it acts preferably as a trivalent or a bivalent element. Then, further, as we have seen, cobalt forms a few compounds in which it is trivalent, but it is generally bivalent, and nickel is scarcely ever trivalent. In its compounds nickel resembles copper in the cupric compounds, and copper is the next element in the order of increasing atomic weights. But copper has an additional power which allies it to the members of Group A, Family I. It acts as a univalent element in the cuprous compounds.

Now, in the same way, there is an increase in the complexity of the compounds formed by the elements, as we pass from zirconium, to niobium, to molybdenum, and below manganese in Family VII we should expect to find an element forming compounds which in general resemble those of manganese, and leading up to the octovalent element ruthenium. Considering the relations between iron and ruthenium, one is tempted to suspect that this unknown element may exhibit a valence of nine in some unstable compounds. While ruthenium is octovalent in its highest oxide, it is also septivalent in $HRuO_4$, sexivalent in $H_2RuO_4$, quadrivalent in $RuO_2$, trivalent in $Ru_2O_3$, and bivalent in $RuO$. Rhodium, however, is only quadrivalent, trivalent, and bivalent; and palladium is quadrivalent, bivalent, and univalent. Just as nickel leads naturally to copper, so palladium leads naturally to silver.

In regard to the series to which osmium, iridium, and platinum belong, not as much is known as in regard to the series just referred to, though the three elements themselves have been carefully studied. There is here observed the same falling off of valence power from osmium to platinum; and just as nickel leads to copper, and palladium leads to silver, so platinum leads naturally to gold in Family I.

## THE PLATINUM METALS.

The six elements of Sub-Groups B and C, Family VIII, are generally grouped together and spoken of as the platinum metals. They occur together in nature, and almost always in alloys, into the composition of which all enter. The chief constituent is platinum, which is present to the extent of 50 to 80 per cent, and over. The alloys occur in only a few localities, in the Ural Mountains, in California, Australia, Borneo, and a few other places, and form small pieces which are mixed with sand and earth. They generally contain also gold, iron, and copper. Palladium occurs, further, in a gold ore which is found in Brazil.

**Metallurgy.**—The process for obtaining the metals from the ores is based mainly upon the following facts: (1) Gold is soluble in dilute *aqua regia*, while platinum requires concentrated *aqua regia;* (2) platinic chloride, $PtCl_4$, and iridium chloride, $IrCl_4$, form, with ammonium chloride, difficultly soluble compounds of the formulas $(NH_4)_2PtCl_6(PtCl_4.2NH_4Cl)$ and $(NH_4)_2IrCl_6(IrCl_4.2NH_4Cl)$. When these compounds are ignited, they are completely decomposed, and the metals are left behind. When, therefore, platinum-ore has been freed as far as possible from sand and earth, it is first treated with dilute *aqua regia*, which removes the gold, and then with concentrated *aqua regia*, which dissolves the platinum together with a little iridium, leaving an alloy of iridium and osmium.

When the solution thus obtained is treated with ammonium chloride, both metals are precipitated; and when the precipitate is ignited, both metals are left behind in the form of a spongy mass. This consists, however, almost wholly of platinum, the amount of iridium being very small.

### RUTHENIUM, Ru (At. Wt. 100.91).

**Preparation.**—Ruthenium is obtained from the residue which is left undissolved when platinum-ore is treated with concentrated nitro-hydrochloric acid.

**Properties.**—When heated in oxygen it burns and forms the oxide, $RuO_2$. It is insoluble in the strong acids, and even in nitro-hydrochloric acid it is almost insoluble. Owing to its power to form salts of ruthenious acid, it is dissolved when heated with potassium hydroxide and an oxidizing agent, such as saltpeter or potassium chlorate, and afterwards treated with water.

**Chlorides.**—When heated in chlorine it forms the di-chloride, $RuCl_2$, and some of the trichloride, $RuCl_3$. The tetrachloride, $RuCl_4$, is known in combination with chlorides of the alkali metals.

**Oxides.**—When ruthenium is heated with potassium hydroxide and saltpeter, *potassium ruthenite*, $K_2RuO_4$, is formed. The acid from which this salt is derived is plainly ruthenious acid, $H_2RuO_4$, and this is related to the oxide, $RuO_3$. Neither the acid nor the anhydride is known, however. When the solution is treated with chlorine the first product is *potassium perruthenite*, $KRuO_4$, which forms a dark green solution, and is iso-morphous with potassium permanganate and potassium perchlorate. By further treatment of the solution with a rapid current of chlorine, *ruthenium peroxide*, $RuO_4$, is formed. This is a volatile crystalline solid, which apparently is not acidic. It is easily reduced to the ses-quioxide, $Ru_2O_3$; and, if heated, it is decomposed with explosion.

The oxides of the formulas $RuO_2$, $Ru_2O_3$, and $RuO$ are not basic, and do not dissolve in acids.

## OSMIUM, Os (At. Wt. 189.55).

**Preparation.**—As stated above, this element is left un-dissolved in the form of an alloy with iridium when plati-num-ore is treated with concentrated nitro-hydrochloric acid. In order to separate it from the iridium, advan-tage is taken of the fact that it forms a volatile peroxide, $OsO_4$, similar to that formed by ruthenium, while iridium does not.

**Properties.**—The metal does not melt at the highest temperatures reached artificially. It has the highest specific gravity of all known substances; is easily oxid-

ized when in finely divided condition; and is converted either by the oxygen of the air or by nitric acid into osmium peroxide, $OsO_4$.

**Chlorides.**—The *dichloride*, $OsCl_2$, and the *tetrachloride*, $OsCl_4$, are formed by treating the metal with chlorine. The *trichloride*, $OsCl_3$, is not known in free condition.

**Oxides.**—The metal as well as the oxides forms the *peroxide*, $OsO_4$, when heated in the air. This is also formed by treating a heated mixture of sodium chloride and the alloy of osmium and iridium with chlorine and water vapor. It is commonly called *osmic acid*, though its acid properties are very weak. Like ruthenium peroxide it is volatile. It sublimes in colorless, lustrous needles, and boils without decomposition at a temperature a little above 100°. It has an intense odor similar to that of chlorine, and its vapor attacks the eyes and respiratory organs somewhat in the same way that chlorine does. It dissolves slowly in water, and reducing agents precipitate the metal from the solution. A solution of osmic acid is used in microscopic work. When injected into the tissues, the parts are hardened and colored.— *Potassium osmite*, $K_2OsO_4$, is formed when a solution of the peroxide in potassium hydroxide is treated with a reducing agent. It is easily decomposed in water solution. —The oxides $OsO$, $OsO_2$, and $Os_2O_3$ have neither acid nor basic properties.

## Rhodium, Rh (At. Wt. 102.23).

Rhodium has no acid properties, and does not form a peroxide corresponding to those of ruthenium and osmium. On the other hand, its oxide, $Rh_2O_3$, is basic. The chloride $RhCl_3$ is readily formed, and it is doubtful whether the di- and tetrachlorides have been made.

## Iridium, Ir (At. Wt. 191.66).

**Preparation.**—The extraction of iridium with platinum and with osmium from platinum-ore was referred to above. In order to separate it from platinum, advantage is taken of the fact that it forms a trichloride, $IrCl_3$,

which with ammonium chloride gives an easily soluble double chloride. The reduction is accomplished either by heating the tetrachloride for some time at 150°, or by treating the insoluble double chloride in water with hydrogen sulphide or with sulphur dioxide. From osmium it is separated by treating with moist chlorine, when, as stated above, the osmium is converted into the peroxide, which being volatile passes over. The residue contains the iridium in the form of the tetrachloride, and this, when treated with potassium chloride, forms the difficulty soluble chloriridate, $K_2IrCl_6$.

**Properties.**—Iridium has a grayish-white color, and resembles polished steel. Its specific gravity is nearly the same as that of osmium, being 22.42. It is harder and more brittle than platinum; melts at a higher temperature; and unless it is finely divided it is not dissolved by nitro-hydrochloric acid. When heated with potassium hydroxide and saltpeter it is converted into the oxide.

**Chlorides.**—When finely divided iridium is treated with nitro-hydrochloric acid it is converted into the *tetrachloride,* $IrCl_4$. When the solution of the tetrachloride is heated it gives off chlorine, and the *dichloride,* $IrCl_2$, is formed. The *trichloride,* $IrCl_3$, is formed when the metal is heated in chlorine gas. Both the tetrachloride and the trichloride form double salts with the chlorides of the alkali metals. Those with the tetrachloride have the general formula $M_2IrCl_6$, or $IrCl_4.2MCl$; while those with the trichloride have the general formula $M_3IrCl_3$, or $IrCl_3.3MCl$. The latter are all soluble in water; of the former, the potassium salt, $K_2IrCl_6$, and the ammonium salt, $(NH_4)_2IrCl_6$, are almost insoluble in water.

**Oxides.**—The oxides have neither acid nor basic properties. The one most easily obtained is the dioxide $IrO_2$. The hydroxides, $Ir(OH)_3$ and $Ir(OH)_4$, are obtained, the former as a black and the latter as a blue precipitate, by treating the chlorides with potassium hydroxide.

## PALLADIUM, Pd (At. Wt. 105.56).

**Preparation.**—The chief source of palladium is a Brazilian gold-ore. From this ore the metal can be obtained by various methods, one of which consists in melting it together with silver, and then treating it with nitric acid, when the silver and palladium dissolve, and the gold remains undissolved. The silver is precipitated as chloride and the palladium as the cyanide, and when the latter is ignited it is decomposed, leaving palladium.

**Properties.**—Palladium resembles iridium and platinum in appearance. Its specific gravity is only about half as great as that of platinum, being 11.5; it is more easily fusible than platinum, and dissolves in nitric acid and in hot concentrated sulphuric acid. The property of palladium which has perhaps attracted most attention is its power to absorb hydrogen, and form—

**Palladium-Hydrogen.**—The formation of this compound was referred to under Hydrogen (which see). The combination takes place even at the ordinary temperature, but best at 100°. If the metal is brought into hydrogen at this temperature, it absorbs more than 900 times its volume, forming an alloy of the composition $Pd_2H$. This alloy has a greater volume and lower specific gravity than the palladium from which it is formed. At 130° it begins to decompose under the atmospheric pressure, but continued heating at a red heat is necessary to decompose it completely. If allowed to lie in contact with the air the hydrogen is oxidized to water. Palladium-hydrogen acts as a strong reducing agent, the hydrogen which it gives up being apparently in the nascent or atomic condition.

**Chlorides.**—When palladium is dissolved in concentrated nitro-hydrochloric acid it is converted into *palladic chloride*, $PdCl_4$, which with the chlorides of the alkali metals forms double salts similar to those formed by iridium tetrachloride, and, as we shall see, by platinic chloride. The tetrachloride is decomposed by evaporation of its solution, giving up chlorine and leaving palladious chloride, $PdCl_2$, which crystallizes, and forms

with the chlorides of the alkali metals double salts of the general formula $M_2PdCl_4$, or $PdCl_2.2MCl$.

**Oxides.**—The point of chief interest presented by the oxides is that in one of them, the *suboxide*, $Pd_2O$, the metal appears as a univalent element. The dioxide or *palladic oxide*, $PdO_2$, has neither acid nor basic properties. The monoxide, or *palladious oxide*, $PdO$, forms unstable salts with acids, an example being the sulphate, $PdSO_4 + 2H_2O$.

## PLATINUM, Pt (At. Wt. 193.41).

**Preparation.**—A general idea of the method of procedure in extracting platinum from its ores was given on p. 722. Thus prepared, however, it always contains iridium, and for some purposes for which platinum is used this is objectionable. In order to purify the metal advantage is taken of the fact that iridium chloride can be converted into a trichloride, which with ammonium chloride forms an easily soluble double salt (see p. 725). The metal as obtained by igniting ammonium platinic chloride forms a gray spongy mass known as *spongy platinum*. When a solution of platinous chloride is boiled with potassium hydroxide, and alcohol gradually added, the salt is reduced, and the platinum is precipitated as an extremely fine powder, known as *platinum black*. When spongy platinum and platinum black are heated to fusion by the oxyhydrogen flame they are converted into the compact variety.

**Properties.**—Platinum is a grayish-white metal resembling polished steel; it can be drawn out into very fine wire; it melts in the flame of the oxyhydrogen blowpipe, and when heated above its melting-point it is volatile; its specific gravity is 21.5. At white heat it can be welded. It is not dissolved by nitric acid, hydrochloric acid, nor sulphuric acid, but it dissolves in nitrohydrochloric acid, forming the acid, $H_2PtCl_6$. Fusing alkalies, and particularly a mixture of caustic potash and saltpeter, act upon it; but the alkaline carbonates do not. In contact with red-hot charcoal and silicon dioxide a compound of silicon and platinum is formed.

Finely divided platinum has to a remarkable extent the power of condensing gases upon its surface. It absorbs, for example, 200 times its own volume of oxygen, and other gases in a similar way. The oxygen thus absorbed is in active condition, and if oxidizable substances are brought in contact with it they are easily oxidized. Thus when a current of hydrogen is allowed to flow against a piece of spongy platinum it takes fire, owing to the presence of the condensed oxygen in the pores of the platinum. Similarly, when sulphur dioxide and oxygen are allowed to flow together over spongy platinum, or even the compact metal, the two gases unite to form sulphur trioxide.

**Applications of Platinum.**—The metal is of the greatest value to the chemist on account of its power to resist the action of high temperatures and of most chemical substances. It is used in the laboratory in the form of wire, foil, crucibles, evaporating-dishes, tubes, etc., etc. From what was said above it cannot be used with alkalies and saltpeter, nor with nitro-hydrochloric acid. Platinum vessels, further, should not be placed upon red-hot charcoal. Metallic salts which are easily reduced, such as those of antimony and bismuth, should not be heated in platinum vessels, as the reduced elements, like silicon, form alloys with the platinum, and these, as a rule, are easily fusible. In the concentration of sulphuric acid on the large scale platinum stills are used. The price of platinum is not as high as that of gold, but much higher than that of silver.

**Alloys of Platinum.**—The only alloy of platinum which is of any special importance is that which it forms with iridium. A small percentage of iridium diminishes the malleability of platinum very markedly, and makes it brittle; it, however, increases its resistance to the action of reagents. An alloy of 90 per cent platinum and 10 per cent iridium has been adopted by the French Government as the best material from which to make normal meters. This alloy is very hard, as elastic as steel, more difficultly fusible than platinum, entirely unchangeable in the air, and is capable of a high polish.

**Chlorides.**—Like palladium, platinum forms two chlorides, *platinous chloride*, $PtCl_2$, and *platinic chloride*, $PtCl_4$. The latter is formed when platinum is dissolved in *aqua regia*, and the solution evaporated to dryness. From its solution in water it crystallizes with ten or five molecules of water. It is soluble in alcohol as well as in water. When the dry substance is heated for some time to 225°–230°, it is decomposed, yielding platinous chloride, which is a grayish-green powder insoluble in water.

**Chlorplatinic Acid,** $H_2PtCl_6$, is formed by direct union of platinic chloride with hydrochloric acid. It crystallizes with six molecules of water, and forms a series of salts called the *chlorplatinates*, to which reference has already been made. Those most commonly met with in the laboratory are the potassium salt, $K_2PtCl_6$, or $PtCl_4.2KCl$, and the ammonium salt, $(NH_4)_2PtCl_6$, or $PtCl_4.2NH_4Cl$, both of which are difficultly soluble in water, and are therefore precipitated when platinic chloride is added to solutions containing potassium or ammonium chloride. The sodium salt is easily soluble in water. Many other chlorplatinates are known, and many crystallize well. Considering the similarity in composition between chlorplatinic acid and fluosilicic acid, the conclusion seems justified that they have the same constitution. The reasons which lead to the belief that the constitution of fluosilicic acid is properly represented by the formula

$$Si \begin{cases} Fl \\ Fl \\ (Fl_2)H \\ (Fl_2)H \end{cases}$$ make it probable that the constitution of

chlorplatinic acid should be represented by a similar

formula, $$Pt \begin{cases} Cl \\ Cl \\ (Cl_2)H \\ (Cl_2)H \end{cases}.$$

Platinous chloride like platinic chloride combines with other chlorides to form double salts, the general formula of which is $M_2PtCl_4$, or $PtCl_2.2MCl$.

**Cyanides.**—Platinum forms a number of beautiful double cyanides derived from an acid of the formula
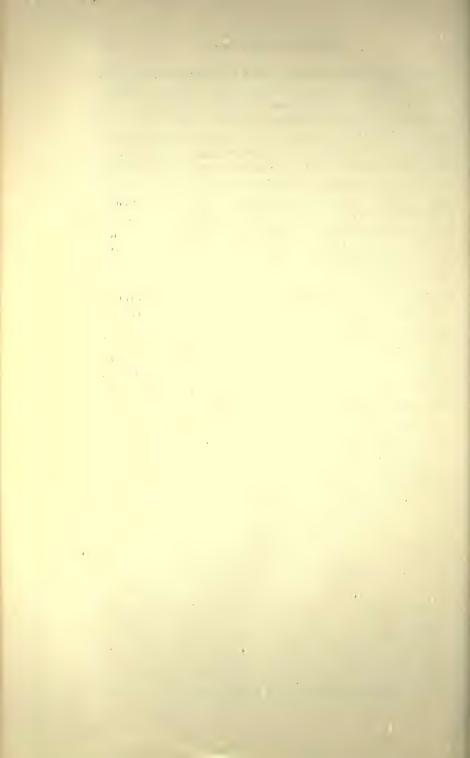
$H_2Pt(CN)_4$ or $Pt(CN)_2.2HCN$, which should be called *cyanplatinous acid*. It is analogous to the acid from which the double chlorides of platinous chloride are derived, $H_2PtCl_4$. These *cyanplatinites* are easily obtained, and, as a rule, crystallize well and are beautifully colored. The *magnesium salt*, $MgPt(CN)_4 + 7H_2O$, forms quadratic prisms, the side faces of which have a green metallic lustre, while the end faces are deep blue.

**Hydroxides and Oxides.**—When a solution of platinic chloride is treated with sodium hydroxide, and afterward with acetic acid, a white precipitate of *platinic hydroxide*, $Pt(OH)_4 + 2H_2O$, is formed, which when dried at 100° loses water and is converted into the brown hydroxide, $Pt(OH)_4$. This loses water when heated higher and is converted into the *oxide*, $PtO_2$. In a similar way *platinous hydroxide*, $Pt(OH)_2$, and platinous oxide, PtO, are obtained from platinous chloride. Platinic hydroxide, $Pt(OH)_4$, has acid properties, and forms a few salts of the general formula $M_2PtO_3$, of which *barium platinate*, $BaPtO_3$, is the best known. *Platinic acid*, from which these salts are derived, is plainly formed from platinic hydroxide by loss of one molecule of water, and bears to it the same relation that ordinary silicic acid, $H_2SiO_3$, bears to normal silicic acid, $Si(OH)_4$. Further, platinic acid and chlorplatinic acid appear to be analogous compounds; and the latter may be regarded as derived from the former by replacement of the three atoms of oxygen by six atoms of chlorine, as shown in the formulas

$$H_2PtO_3 ; \qquad\qquad H_2PtCl_6 ;$$

$$Pt \begin{cases} O \\ OH \\ OH \end{cases} ; \qquad\qquad Pt \begin{cases} Cl \\ Cl \\ (Cl_2)H \\ (Cl_2)H \end{cases} .$$

**Sulphides.**—There are two sulphides of platinum which are analogous to the two oxides, PtO and $PtO_2$. These are *platinous sulphide*, PtS, and *platinic sulphide*, $PtS_2$. They are black insoluble compounds, which are precipitated when hydrogen sulphide or soluble sulphides are added to solutions of platinous and platinic chlorides.

**Compounds with Ammonia—The Platinum Bases.**—Like cobalt salts, the salts of platinum form a large number of compounds with ammonia. When ammonia acts upon a solution of platinous chloride a compound of the formula $PtCl_2(NH_3)_2$ is formed. This is the starting-point for a series of compounds, as the bromide, $PtBr_2(NH_3)_2$; the nitrate, $Pt(NO_3)_2(NH_3)_2$; the sulphate, $PtSO_4(NH_3)_2$; etc. There is another series beginning with the chloride, $PtCl_2(NH_3)_3$; another beginning with the chloride, $PtCl_2(NH_3)_4$. All the above are to be regarded as derived from platinous chloride. Similarly there are other series obtained from platinic chloride. The chlorides have the formulas $PtCl_4(NH_3)_2$, $PtCl_4(NH_3)_3$, $PtCl_4(NH_3)_4$. It seems probable that these salts are ammonium salts in which a part of the hydrogen of the ammonium is replaced by platinum. Thus the chloride $PtCl_2(NH_3)_2$ probably has the constitution $Pt{<}^{NH_3Cl}_{NH_3Cl}$. Although a great deal of work has been done on these platino-ammonium compounds, and much interesting information in regard to them has been gained, the subject of their constitution is still in an unsatisfactory state.

# APPENDIX I

## CONTAINING SPECIAL DIRECTIONS FOR LABORATORY WORK.

**Introduction.**—In order to become familiar with the principles of Chemistry it is absolutely necessary that the student should devote a part of his time to work in the laboratory— the more the better. It is, further, necessary that the laboratory work should be done with the greatest care. Every piece of apparatus should be carefully constructed, the desk should be kept clean and in good order; and no work should be abandoned until the student is satisfied that he has seen all there is to be seen, and that he has learned all that the work can teach him. He must learn to use his own senses, and to believe what he sees, and not simply "what the book says." It sometimes happens that owing to the peculiar way in which an experiment is performed results quite different from those anticipated are obtained. Under these circumstances it is not advisable to conclude at once that "the book must be wrong." It may be; but the probabilities are against this explanation of the discrepancy. Nothing is more instructive than well-directed efforts to find the causes of difficulties. Such efforts, more than anything else, develop the spirit of true scientific inquiry. It is advisable for the student to carry on the work for which directions are given below in connection with the study of the book. A good plan to follow is to read a chapter with care; then to perform the experiments which are intended to illustrate that chapter, and, while doing the work, again to read; and afterwards to write out an account of what has been done, noting everything of importance exactly as it was observed. If experiments are necessary to account for phenomena not described in the book, these should be described; and if a conclusion is reached in regard to these phenomena, the evidence upon which the conclusion is based should be clearly stated. It is only by patient work carried on in this way that one can hope to reach a clear conception of the science. But by such work the desired result will be reached.

Progress will seem slow at first, as it always does in a new subject; but in time the ideas will begin to arrange themselves systematically, order will come out of confusion, and in this result the conscientious student will find a delightful reward for his labor.   Every great branch of knowledge is made up of details which are bound together by certain broad governing principles.   It is impossible to avoid these details.   In order to understand the governing principles the details must be studied to some extent.   They form the raw material from which the science is constructed; without them the science would be impossible.   As well might one hope to learn a language by studying its grammatical rules and avoiding the details of the mere words, as to learn chemistry by studying the laws and avoiding contact with the things to which these laws have reference.

## EXPERIMENTS TO ACCOMPANY CHAPTER I.

### Chemical Change caused by Heat.

**Experiment 1.**—In a clean *dry* test-tube put enough white sugar to make a layer $\frac{1}{4}$ to $\frac{1}{2}$ an inch thick.   Hold the tube in the flame of a spirit-lamp or a laboratory burner.   What evidence is furnished by this experiment that chemical change may be caused by heat?   What is left in the tube?   Is it soluble?   Is it sweet?   Is it sugar?

**Experiment 2.**—Half-fill the bulb of an arsenic-tube with red oxide of mercury, or, if such a tube is not available, proceed as follows: From a piece of hard-glass tubing of about 6 to 7 millimeters ($\frac{1}{4}$ inch) internal diameter cut off a piece about 10 centimeters (4 inches) long by making a mark across it with a triangular file, and then seizing it with both hands, one on each side of the mark, pulling and at the same time pressing slightly as if to break it.   Clean and dry it, and hold one end in the flame of a blast-lamp until it melts together.   During the melting turn the tube constantly around its long axis so that the heat may act uniformly upon it.   Put into the tube thus made enough red oxide of mercury (mercuric oxide) to form a layer about 12 millimeters ($\frac{1}{2}$ inch) thick.   Heat the tube as in the last experiment.   What change in color is noticed?   What is deposited upon the glass in the upper part of the tube?   What evidence is

furnished by this experiment that chemical change can be effected by heat?

## Chemical Changes can be effected by an Electric Current.

**Experiment 3.**—To the ends of insulated copper wires connected with two cells of a Bunsen's or Grove's battery fasten platinum plates, say 25 mm. (1 inch) long by 12 mm. ($\frac{1}{2}$ inch) wide. Insert these platinum electrodes into water contained in a shallow glass vessel about 15 cm. (6 inches) wide and 7 to 8 cm. (3 inches) deep, taking care to keep them separated from each other. No action will take place, for the reason, as has been shown, that water will not conduct the current, and hence when the platinum electrodes are kept apart there is no current. By adding to the water about one tenth its own volume of strong sulphuric acid it acquires the power to convey the current. It will then be observed that bubbles rise from each of the platinum plates. In order to collect them an apparatus like that shown in Fig. 15 may be used.

*h* and *o* represent glass tubes which may conveniently be about 30 cm. (1 foot) long and 25 mm. (1 inch) internal diameter. They are first filled with the water containing one tenth its volume of sulphuric acid, and then placed with the mouth under water in the vessel *A*. The platinum elec-



trodes are now brought beneath the inverted tubes. The bubbles which rise from them will pass upward in the tubes and the water will be pressed down. Gradually the water will be completely forced out of one of the tubes, while the other is still half full of water. The substances thus collected in the tubes are invisible gases. After the first tube is full of gas, place the thumb over its mouth and remove the tube. Turn it mouth upward, and at once apply a lighted match to it. A flame will be noticed. The gas which was contained in the tube is therefore capable of burning. It cannot, therefore, have been air. In the mean time the second tube will
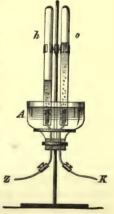
Fig. 15.

have become filled with gas. Remove this tube in the same way and insert a thin piece of wood with a spark on it. The spark will at once burst into flame, and the burning of the

wood will take place more actively than it does in ordinary air, as may be shown by withdrawing it and again inserting it into the tube. The gas in this tube, it will be noticed, does not take fire. Without going into further details, it is clear from the above experiment that when an electric current acts on water two invisible gases are produced. A chemical change is caused by an electric current.

### Mechanical Mixtures and Chemical Compounds.

**Experiment 4.**—Examine carefully a piece of coarse-grained granite; break off some of it, and separate the constituents. How many are there? By what properties do you recognize them? Powder a small bit of one of the constituents, and examine the powder with the microscope. Do you recognize more than one kind of matter? Mix the powder of the three constituents, and see whether in the mixed powder there is any difficulty in detecting the three kinds of matter with the aid of the microscope.

**Experiment 5.**—Mix a gram or two of powdered roll-sulphur and an equal weight of very fine iron filings in a small mortar. Examine a little of the mixture with a microscope. Not only can we recognize the particles of iron and of sulphur by means of the microscope, but we can also pick out the pieces of iron by means of a magnet. The magnet attracts the iron but not the sulphur, so that by passing the magnet often enough through the mixture we can pick out all the iron and leave all the sulphur. This separation is really a mechanical separation. It is only a somewhat more refined method of picking out than that used in the case of granite.

**Experiment 6.**—Pass a small magnet through the mixture above prepared. Unless the substances used are thoroughly dry, particles of sulphur will adhere to the magnet, but even then it will be seen that most of that which is taken out of the mixture is iron.

The iron and sulphur can also be separated by treating the mixture with a liquid known as carbon disulphide. Sulphur dissolves in this liquid, but iron does not. So that when the mixture is treated with it the iron is left behind, and can easily be recognized as such.

**Experiment 7.**—Pour two or three cubic centimeters of carbon disulphide on a little powdered *roll-sulphur* in a dry test-tube. The sulphur dissolves. Treat iron filings in the

same way. The iron does not dissolve. Now treat a small quantity of the mixture with carbon disulphide. After the sulphur is dissolved pour off the solution on a good-sized watch-glass and let it stand. Examine what remains undissolved in the test-tube, and satisfy yourself that it is iron. After the liquid has evaporated examine what is left in the watch-glass and satisfy yourself that it is sulphur. Why are you justified in concluding that the substance left in the test-tube is iron and that left on the watch-glass is sulphur?

**Experiment 8.**—Make a fresh mixture of three grams each of powdered roll-sulphur and fine iron filings. Grind them together intimately in a dry mortar and put them in a dry test-tube. Heat gradually until the mass begins to glow. At first the sulphur melts and becomes dark-colored. It may even take fire. But soon something else evidently takes place. The whole mass begins to glow, and if you at once take the tube out of the flame, the mass continues to glow, becoming brighter. This soon stops; the mass grows dark and gradually cools down. As soon as it reaches the ordinary temperature, the tube should be broken and the contents put in a mortar. A close examination will show that the mass does not look like the mixture of sulphur and iron with which we started. It has a bluish-black color, and is apparently homogeneous. An examination with the microscope, the magnet, and carbon disulphide will prove that, while there may be a little iron left, and possibly a little sulphur, most of the bluish-black mass is neither iron nor sulphur, but a new substance with properties quite different from those of iron and from those of sulphur.

## OTHER EXAMPLES OF CHEMICAL ACTION.

**Experiment 9.**—Examine a piece of calc-spar or marble. You see that it is made up of pieces of definite shape. It is, as we say, crystallized. It is quite hard, though a knife will cut it. Heated in a hard-glass tube, as in Experiment 2, it does not melt, but remains essentially unchanged. It does not dissolve in water. To prove this, put a piece the size of a pea in a test-tube with pure water. Thoroughly shake, and then, as heating usually aids solution, boil. Now pour off a few drops of the liquid on a piece of platinum-foil or a watch-glass, and by gently heating cause the water to evaporate. If there is anything in solution, there will be a solid residue on

the platinum-foil or watch-glass. If not, there will be no residue. Now treat a small piece of the substance with dilute hydrochloric acid and notice what takes place. Bubbles of gas are given off. After the action has continued for about a minute, insert a lighted match in the upper part of the tube. It is extinguished, and the gas does not burn. The gas formed in this case is therefore plainly not identical with either one of those obtained from water by the action of the electric current (see Experiment 3). It is what is commonly called carbonic-acid gas. As the action continues, the piece of calc-spar or marble grows smaller and smaller, and finally disappears, when there is a clear solution. The substance has dissolved in the hydrochloric acid. In order to determine whether anything else has taken place besides the dissolving, we shall have to get rid of the excess of hydrochloric acid. This we can easily do by boiling it, when it passes off in the form of vapor, and then whatever is in solution will remain behind. For this purpose put the solution in a small, clean porcelain evaporating-dish, and put this on a vessel containing boiling water, or a water-bath. The operation should be carried on in a place in which the draught is good, so that the vapors will not collect in the working-room. They are not poisonous, but they are annoying. The arrangement for evaporating is represented in Fig. 16.

After the liquid has evaporated and the substance in the

evaporating-dish is dry, examine it, and carefully compare its properties with those of the substance which was put into the test-tube. Its structure will be found not to present the regularities noticed in the original substance. It is much softer, dissolves in water, melts when heated in a hard-glass tube. It does not give off a gas when treated with hydrochloric acid. When exposed to the air it soon becomes moist, and after a time liquid. The experiment shows that when hydrochloric acid acts upon calc-spar or marble the latter at least loses its own properties. It might be shown that some of the hydrochloric acid also loses its properties. In place of the two we get a new

substance with entirely different properties. The two substances have acted chemically upon each other and produced a chemical compound. In this case it was only necessary to bring the substances in contact in order to cause them to act chemically upon each other. It was not necessary to heat them, as it was in the case of the iron and sulphur.

**Experiment 10.**—Bring together in a test-tube a small piece of copper and some moderately dilute nitric acid. In a short time action begins. The upper part of the tube becomes filled with a dark, reddish-brown gas which has a disagreeable smell. Do not inhale it, as when taken into the lungs it produces bad effects. The solution becomes colored dark blue, and the copper disappears. Examine this solution, as in Experiment 9, and see what has been formed. What are the properties of the substance found after evaporation of the liquid? Is it colored? Is it soluble in water? Does it change when heated in a tube? Is it hard or soft? Does it in any way suggest the copper with which you started?

**Experiment 11.**—Try the action of dilute sulphuric acid on a little zinc in a test-tube. A gas will be given off. Apply a lighted match to it. Does the result suggest anything noticed in an experiment already performed? After the zinc has disappeared, evaporate the solution as in Experiment 9. Carefully compare the properties of the substance left behind with those of zinc.

**Experiment 12.**—Hold the end of a piece of magnesium ribbon about 20 centimeters (8 inches) long in a flame until it takes fire; then hold the burning substance quietly over a piece of dark paper, so that the light, white product may be collected. Compare the properties of this white product with those of the magnesium. Here again a chemical act has taken place. The magnesium has combined with something which it found in the air, and heat was produced by the combination. The product is the white substance.

**Experiment 13.**—In a small, dry flask (400 to 500 ccm.) put a bit of granulated tin. Pour upon it 2 or 3 ccm. concentrated nitric acid. If no change takes place, heat gently, and presently there will be a copious evolution of a reddish-brown gas with a disagreeable smell, (under what conditions has a gas like this already been obtained?) the tin will disappear, and in its place will appear a white powder. Compare the

properties of this white powder with those of tin.    Why are
you justified in concluding that they are not the same thing?

## EXPERIMENTS TO ACCOMPANY CHAPTER II.

### PREPARATION OF OXYGEN.

**Experiment 14.**—Make a small quantity of oxygen by
heating strongly an arsenic-tube half-filled with manganese
dioxide and fitted with a small rubber delivery-tube.

**Experiment 15.**—Make some oxygen by heating a few
grams of mercuric oxide in a hard-glass tube closed at one
end and connected at the other end by means of a cork with
a bent glass tube.

**Experiment 16.**—Arrange an apparatus as shown in Fig.
17.    *A* represents a flask of 100 ccm. capacity.    By means of
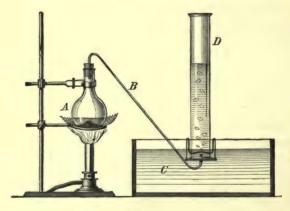


FIG. 17.

a well-fitting rubber stopper one end of the bent-glass tube *B*
is connected with it, and the other end, which should turn
upward slightly, is placed under the surface of the water in *C*.
In *A* put 4 to 5 grams (about an eighth of an ounce) potas-
sium chlorate, and gently heat by means of the lamp.    Notice
carefully what takes place.    At first the potassium chlorate
will melt, forming a clear liquid.    If the heat is increased,
the liquid will appear to boil, and it will soon be seen that a
gas is given off.    Now bring the inverted cylinder *D* filled
with water over the end of the tube, and let the bubbles

of gas rise in the cylinder. After a considerable quantity of gas has been collected in this way the action stops, the mass in the flask becomes solid, and apparently the end of the process is reached. But if the heat is raised again, gas will again begin to come off, and in this second stage a larger quantity will be collected than in the first. Finally, however, the end is reached, and the substance left in the flask remains unchanged, no matter how long heat may be applied. An examination of the gas collected will show that a piece of wood will burn in it very readily. Explain the changes which have taken place in this experiment. Calculate how much oxygen can be obtained by heating 12 grams of potassium chlorate.

## MEASUREMENT OF THE VOLUME OF GASES.

In studying chemical changes it often becomes necessary to measure the volume of a gas, and it is important to know what precautions must be taken in such cases. For the purpose a tube is used which is graduated by marks etched on the outside. These marks may either indicate the number of cubic centimeters of gas contained in the tube, or the length of the column of gas. In the latter case it is of course necessary to determine what volume corresponds to a given length of the column. The chief difficulty encountered in measuring gas volumes is due to the fact that the volume varies with the temperature and pressure. When the temperature of a gas is raised one degree centigrade its volume is increased $\frac{1}{273}$ part. If, therefore, the volume of a gas at $0°$ is $V$, at $t°$ its volume $V'$ will be

$$V + \frac{t}{273} V, \quad \text{or} \quad V' = \frac{V(273 + t)}{273}.$$

This expression may also be written thus:

$$V' = V + 0.00366t \cdot V, \quad \text{or} \quad V' = V(1 + 0.00366t).$$

From these we get the expressions

$$V = \frac{273 V'}{273 + t} \quad \text{and} \quad V = \frac{V'}{1 + 0.00366t}.$$

It is customary to reduce the observed volume of a gas to the volume which it would have at $0°$. The correction is easily

made by the aid of the above formula. Thus, if the volume of a gas is found to be 250 cubic centimeters at 15°, and it is required to know what the volume would be if the temperature were reduced to 0°, the calculation is made thus : In this case the observed volume $V'$ is 250 cc.; $t$, the temperature, is 15°. Substituting these values in the equation

$$V = \frac{273\,V'}{273 + t}, \quad \text{or} \quad V = \frac{V'}{1 + 0.00366t},$$

we have

$$V = \frac{273 \times 250}{273 + 15}, \quad \text{or} \quad V = \frac{250}{1 + 0.00366 \times 15},$$

from which we get 236.99 as the value of $V$.

But the volume of a gas varies also according to the pressure. If the pressure is doubled, the volume is decreased one half ; and if the pressure is decreased one half, the volume is doubled, and so on. In other words, the volume of a gas varies inversely according to the pressure. Increase the pressure two, three, or four times, and the volume becomes one half, one third, or one fourth, and *vice versa*. If the gas has the volume $V$ at the pressure $P$, and at pressure $P'$ the volume $V'$, these values are found to bear to one another the relations expressed in the equation

$$VP = V'P'.$$

The pressure is usually stated in millimeters, and reference is to the height of a column of mercury which the pressure corresponds to. A gas contained in an open vessel, or in a vessel over mercury or water, in which the level of the liquid inside and outside the vessel is the same, is under the pressure of the atmosphere. What that is we learn from the barometer. As this pressure varies, it is necessary to read the barometer whenever a gas is measured, and then to reduce the observed volume to certain conditions which are accepted as standard. If the gas is measured in a tube over mercury or water, and the level of the liquid inside the tube is higher than that outside, the gas is under diminished pressure, the amount of diminution depending on the height of the column of mer-

cury or water in the tube. Thus, if the arrangement is as
represented in Fig. 18, the height
of the mercury column above the
level of the mercury in the trough be-
ing 100 millimeters, and the pressure
of the atmosphere 760 millimeters
of mercury; then the gas in the tube
is plainly not under the full atmos-
pheric pressure, for the atmosphere
is supporting a column of mercury
100 millimeters high, and the pres-
sure actually brought to bear on the
gas corresponds to $760 - 100 = 660$
mm. of mercury. Suppose that in
this case the volume of gas actually
measured is 75 cc. Call this $V$.



FIG. 18.

What would be the actual volume $V$ under the standard 760
mm.? We have seen that

$$VP = V'P'.$$

Now, in this case $P = 760$, $V' = 75$, and $P' = 660$. There-
fore, $760 \, V = 75 \times 660$, or $V = \dfrac{75 \times 660}{760} = 65.13$.

In all cases it is necessary to make a correction similar to
this in dealing with the volumes of gases. The correction for
temperature and that for pressure may be made in one opera-
tion, the formula being

$$V = \frac{273 \, V'P'}{760(273 + t)}, \quad \text{or} \quad V = \frac{V'P'}{760(1 + 0.00366t)},$$
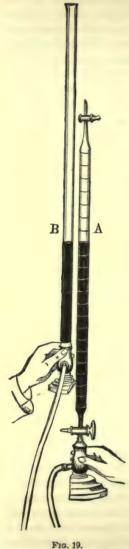
in which $V =$ the volume of the gas at 0° and 760 mm. pres-
sure; $V' =$ the observed volume; $t =$ the observed temper-
ature; $P' =$ the pressure under which the gas is measured.
Some of the most important ideas which have been intro-
duced into chemistry with a view of explaining the regularities
observed in the quantities of substances which act upon one
another chemically have their origin in observations on the
conduct of gases. It is therefore of the highest importance
that the student should familiarize himself with the meaning
of the expression, " the volume of a gas under standard condi-
tions." The presence of water vapor in a gas also influences

its volume, and this must be taken into account in refined work. The formula for making all the corrections required in determining the volume of a gas is

$$V = \frac{273\,V'(P'-a)}{760(273+t)}, \quad \text{or} \quad V = \frac{V'(P'-a)}{760(1+0.00366t)}.$$

in which the letters $V$, $V'$, $P'$, and $t$ have the same significance as in the last formula given, while $a$ is the tension of water vapor at $t°$.

A convenient apparatus for measuring gas volumes, which simplifies the process, is that represented in Fig. 19. It consists of two tubes connected at the base by means of a piece of rubber tubing, and containing water. The tube $A$ is graduated, the other is not. The gas the volume of which is to be measured is brought into the tube $A$, with the narrow opening at the top, and the other tube is then placed at the side of the one containing the gas, and its height adjusted so that the column of liquid in both tubes is at the same level. Under these circumstances, obviously, the gas is under the atmospheric pressure for which the necessary correction must of course be made. It is also necessary in this case to make the corrections for temperature and the tension of aqueous vapor. It is, further, sometimes convenient when the gas is measured over water to transfer the measuring-tube to a vessel containing enough water to permit the immersion of the tube to a point at which the level of the liquid inside and outside of the tube is the same. In this case the conditions are the same as in the apparatus described in the last paragraph. The arrangement is represented in Fig. 20.



FIG. 19.

## DETERMINATION OF THE AMOUNT OF OXYGEN LIBERATED WHEN A KNOWN WEIGHT OF POTASSIUM CHLORATE IS DECOMPOSED BY HEAT.

**Experiment 17.**—To determine how much oxygen is given off when a known weight of potassium chlorate is decomposed by heat, proceed as follows: In a small dry hard-glass tube about 10 cm. long and 5 to 7 mm. internal diameter, closed at one end, weigh out on a chemical balance about 0.25 gram dry potassium chlorate, first weighing the tube empty. Introduce just above the potassium chlorate a plug of asbestos which has been ignited, then, by means of a blast-lamp, soften the upper end of the tube, and draw it out so that it has the form shown in Fig. 21. Now weigh the tube again.
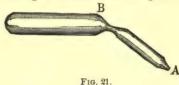
Let

$a$ = weight of tube empty ;

$b$ = weight of tube with potassium chlorate ;

$c$ = weight of tube with potassium chlorate and plug.

Connect at $A$ by means of a short piece of rubber tubing with the measuring tube Fig. 19



FIG. 20.          FIG. 21.

so that the ends of the two tubes are almost in contact with each other, the measuring tube having been previously filled with water to the zero point, and the top closed by means of the stop-cock. Open the stop-cock, and now heat the potassium chlorate gently at first, and gradually higher until no more gas is given off. After the gas has stood for half an hour to cool it down to the temperature of the air, adjust the two tubes of the measuring apparatus so that the level of the water in both is the same; read off the volume of gas. At the same time read the barometer and thermometer; and now make the corrections for pressure and temperature as above directed. The weight of a liter or 1000 cc. of oxygen at 0° and 760 mm. pressure is 1.4290 grams. Knowing the volume of oxygen obtained, calculate the weight of this volume.

Remove the tube containing the product left after the decomposition of the potassium chlorate, and weigh it.

Let

$d$ = weight of tube after decomposition of potassium chlorate.
Now

$b - a$ = weight of potassium chlorate used ;

$d - (a + c - b)$ = weight of potassium chloride left.

Knowing further the weight of the oxygen obtained in the decomposition, which we may call $e$, it is obvious from what has been said that

$$d - (a + c - b) + e \text{ should be equal to } b - a,$$

and the weights should all be in accordance with the equation

$$KClO_3 = KCl + 3O.$$

Make all the calculations, and see how nearly the results obtained agree with what is required by this equation. Should the results not be satisfactory the first time, repeat the work. The more carefully the work is done, the more nearly will the results agree with the equation.

**Experiment 18.**—Mix 25 to 30 grams (or about an ounce) of potassium chlorate with an equal weight of manganese di-
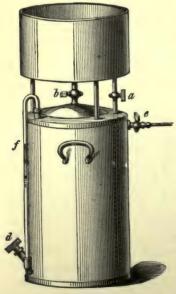


FIG. 22.

oxide in a mortar. The substances need not be in the form of powder. Heat the mixture in a glass retort, and collect the gas by displacement of water in appropriate vessels,—cylinders, bell-glasses, bottles with wide mouths, etc. It will also be well to collect some in a gasometer, such as is commonly found in chemical laboratories, the essential features of which are represented in Fig. 22. It is made either of metal or of glass. The opening at $d$ can be closed by means of a screw cap. In order to fill it with water, open the stop-cocks and pour the water into the upper part of the vessel after having screwed on the cap $d$. When it is

full, water will flow out of the small tube *e.* Now close all the stop cocks, and remove the cap *d.* The water will stay in the vessel for the same reason that it will stay in a cylinder inverted with its mouth below water. To fill the gasometer with gas, put it over a tub or sink, and introduce the tube from which gas is issuing into the opening at *d.* The gas will rise and displace the water, which will flow out at *d.* When full, put the cap on. To get the gas out of the gasometer, attach a rubber tube to *e,* pour water into the upper part of the gasometer, open the stop-cock *a* and that at *e,* when the gas will flow out, and the current can be regulated by means of the stop-cock at *e.*

The arrangement of the retort is shown in Fig. 23.
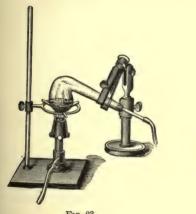
FIG. 23.      FIG. 24.

## PHYSICAL PROPERTIES OF OXYGEN.

**Experiment 19.**—Inhale a little of the gas from one of the bottles. Has it any taste? any odor? any color?

## CHEMICAL PROPERTIES OF OXYGEN.

**Experiment 20.**—Turn three of the bottles containing oxygen with the mouth upward, leaving them covered with glass plates. Into one introduce some sulphur in a so-called deflagrating-spoon, which is a small cup of iron or brass attached to a stout wire which passes through a metal plate, usually of tin (see Fig. 24). In another put a little char-

coal (carbon), and in a third a piece of phosphorus * about the size of a pea. Let them stand quietly, and notice what changes, if any, take place. Sulphur, carbon, and phosphorus are elements, and oxygen is an element. It will be noticed that the sulphur and the carbon remain unchanged, while some change is taking place in the vessel containing the phosphorus, as is shown by the appearance of white fumes. After some time the phosphorus will disappear entirely, the fumes will also disappear, and there will be nothing to show us what has become of the phosphorus. If the temperature of the room is rather high, it may happen that the phosphorus takes fire. If it should, it will burn with an intensely bright light. After the burning has stopped, the vessel will be filled with white fumes, but these will quickly disappear, and the vessel will apparently be empty. What do these experiments prove with reference to the action of oxygen on sulphur, carbon, and phosphorus at the ordinary temperature?

**Experiment 21.**—In a deflagrating-spoon set fire to a little sulphur and let it burn in the air. Notice whether it burns with ease or with difficulty. Notice the odor of the fumes which are given off. Now set fire to another small portion, and introduce it in a spoon into one of the vessels containing oxygen. It will be seen that the sulphur burns much more readily in the oxygen than in the air. Notice the odor of the fumes given off. Is it the same as that noticed when the burning takes place in the air?

**Experiment 22.**—Perform similar experiments with charcoal.

**Experiment 23.**—Burn a piece of phosphorus *not larger than a pea* in the air and in oxygen. In the latter case the light emitted from the burning phosphorus is so intense that it is painful to some eyes. It is better to be cautious. The phenomenon is an extremely brilliant one. The walls of the vessel in which the burning takes place become cov-

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* Phosphorus should be handled with great care. It is always kept under water, usually in the form of sticks. If a small piece is wanted, take out a stick with a pair of forceps, and put it under water in an evaporating-dish. *While it is under the water*, cut off a piece of the size wanted. Take this out by means of a pair of forceps, lay it for a moment on a piece of filter-paper, which will absorb most of the water; then quickly put it in the spoon.

ered with a white substance, which afterwards gradually disappears.

What differences do you notice between the burning in the air and in oxygen? In the experiments is there any sulphur, or carbon, or phosphorus left behind? Do the experiments furnish any evidence that oxygen takes part in the action? or that oxygen is used up?

**Experiment 24.**—Straighten a steel watch-spring,* and fasten it in a piece of metal—such as is used for fixing a deflagrating-spoon in an upright position; wind a little thread around the lower end, and dip it in melted sulphur. Set fire to this, and insert it into a vessel containing oxygen. For a moment the sulphur will burn as in Experiment 21; but soon the steel begins to burn brilliantly, and the burning continues as long as there is oxygen left in the vessel. Notice that in this case *there is no flame,* but instead very hot particles are given off from the burning iron. The phenomenon is of great beauty, especially if observed in a dark room. The walls of the vessel become covered with a dark reddish-brown substance, some of which will also be found at the bottom in larger pieces.

## Oxygen is used up in Combustion.
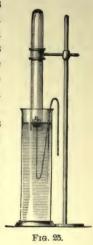
**Experiment 25.**—Is the odor of the contents of the bottle in which the sulphur was burned the same as before the experiment? Introduce a stick with a small flame on it successively into the vessels used in burning sulphur, carbon, phosphorus, and iron. Is oxygen present or not? What evidence have you on this point?

**Experiment 26.**—Fill a tube say 30 to 40 cm. (12 to 15 inches) long, and $2\frac{1}{2}$ to 3 cm. (1 to $1\frac{1}{4}$ inches) wide, with oxygen, and arrange it in a vessel over water, as shown in Fig. 25. Now fasten a small stick of phosphorus to the end of a wire and push it into the tube so that about $\frac{1}{4}$ to $\frac{1}{2}$ inch of the phosphorus is above the water and exposed to the oxygen. At first no action will take place, but after a

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* Old watch-springs can generally be had of any watch maker or mender for the asking. A spring can be straightened by unrolling it, attaching a weight, and suspending the weight by the spring. The spring is then heated up and down to redness with the flame of a Bunsen burner.

time white fumes will be seen to rise from the phosphorus, and the phosphorus will begin to melt. This action will be accompanied by a diminution of the volume of the oxygen, as will be shown by the rise of the water. When the water has risen so as to cover the phosphorus, shove the stick up so that it is again just above the surface of the water. Some of the oxygen will again be used up. By working carefully, and repeating this process as many times as may be necessary, the oxygen can all be used up without the active burning of the phosphorus. Usually, however, before the action is completed, the temperature of the phosphorus becomes so high that it takes fire, when there is a flash of light in the tube and a sudden rise of the water, showing that the gas is suddenly used up.

Fig. 25.

**Experiment 27.**—Burn a steel watch-spring as directed in Experiment 24, with the difference that the spring is passed air-tight through a cork which is fitted tightly into the neck of the bell-jar. As the spring burns, the water will rise from the vessel in which the bell-jar is standing, and it is necessary to pour water into this vessel. When the spring has burned near to the cork shove it through so that the burning may continue. If the experiment is properly performed the bell-jar will be nearly full of water at the end. What does this prove?

## The Products of Combustion weigh more than the Body Burned.

Fig. 26.

**Experiment 28.**—Weigh off about a gram of magnesium ribbon in a porcelain crucible. Heat over a Bunsen burner until the magnesium has turned to a white substance (magnesium oxide). After cooling, weigh again. Perform the same experiment with zinc, tin, and lead. What conclusion are you justified in drawing?

**Experiment 29.**—Over each pan of a large and rather sensitive balance suspend a glass tube filled with pieces of solid

caustic soda. A balance that will answer the purpose very well can be made of wood with metal bearings. It may conveniently be about $2\frac{1}{2}$ feet high, with a delicate beam about 3 feet long. The best tubes for the caustic soda are Argand lamp-chimneys, around the bottom of which is tied a piece of wire-gauze to prevent the caustic soda from falling out. On one pan of the balance place a candle directly under one of the caustic-soda tubes, so adjusted that the flame shall be not more than $2\frac{1}{2}$ to 3 inches below the bottom of the tube. By means of weights placed on the other pan establish equilibrium. Now light the candle. Slowly, as it burns, the pan upon which it is placed will sink, showing that the products of combustion which are partly absorbed by the caustic soda are heavier than the candle was. While this is by no means an accurate experiment, it is a very striking one, and proves beyond question that in the process of combustion matter is taken up by the burning body.

## EXPERIMENTS TO ACCOMPANY CHAPTER III.

### PREPARATION OF HYDROGEN.

**Experiment 30.**—Repeat Experiment 3 and examine the gases.

**Experiment 31.**—Throw a small piece of sodium * on water. While it is floating on the surface apply a lighted match to it. A yellow flame will appear. This is burning hydrogen, the flame being colored yellow by the presence of the sodium, some of which also burns. Make the same experiment with potassium. The flame appears in this case without the aid of the match. It has a violet color, which is due to the burning of some of the potassium. The gas given off in these experiments is either burned at once or escapes into the air. In the case of the potassium it takes fire at once, because the action takes place rapidly and the heat evolved is sufficient to set fire to it; in the case of the sodium, however, the action takes place more slowly, and the temperature does not get high enough to set fire to the gas. In order to collect it unburned, it is only necessary to allow the decomposition to take place so that the

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* The metals sodium and potassium are kept under oil. When a small piece is wanted take out one of the larger pieces from the bottle, roughly wipe off the oil with filter-paper, and cut off a piece the size needed. It is not advisable to use a piece larger than a small pea.

gas will rise in an inverted vessel filled with water. For this purpose fill a good-sized test-tube with water and invert it in a vessel of water. Cut off a piece of sodium not larger than a pea, wrap it in a layer or two of filter-paper, and with the fingers or a pair of curved forceps bring it quickly below the mouth of the test-tube and let go of it. It will rise to the top, the decomposition of the water will take place quietly, and the gas formed, being unable to escape, will remain in the tube. By repeating this operation in the same tube a second portion of gas can be made, and so on until the vessel is full.

Examine the gas and see whether it acts like the hydrogen obtained from water by means of the electric current. What evidence have you that they are the same? Is this evidence sufficient to prove the identity of the two?

The metals sodium and potassium disappear in these experiments, and we get hydrogen. What becomes of the metals? and what is the source of the hydrogen? If after the action has stopped the water is examined, it will be found to contain something in solution. It now has a peculiar taste, which we call alkaline; it feels slightly soapy to the touch; it changes certain vegetable colors. If the water is evaporated off, a white substance remains behind, which is plainly neither sodium nor potassium. In solid form or in very concentrated solution it acts very strongly on animal and vegetable substances, disintegrating many of them. On account of this action it is known as *caustic* soda, or, in the case of potassium, as *caustic* potassa.
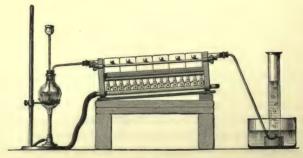


FIG. 27.

**Experiment 32.**—Certain metals which do not decompose water at ordinary temperatures, or which decompose it slowly, decompose it easily at elevated temperatures. This is true of

iron. If steam is passed through a tube containing pieces of iron heated to redness, decomposition of the water takes place, and the oxygen is retained by the iron, which enters into combination with it, while the hydrogen is liberated. In this experiment a porcelain tube with an internal diameter of from 20 to 25 mm. (about an inch) and a gas furnace are desirable, though a hard-glass tube and a charcoal furnace will answer. The arrangement of the apparatus is shown in Fig. 27.

**Experiment 33.**—In a cylinder or test-tube put some small pieces of zinc, and pour upon it some ordinary hydrochloric acid. If the action is brisk, after it has continued for a minute or two apply a lighted match to the mouth of the vessel. The gas will take fire and burn. If sulphuric acid diluted with five or six times its volume of water* is used instead of hydrochloric acid, the same result will be reached. The gas evolved is hydrogen. For the purpose of collecting the gas the operation is best performed in a wide-mouthed bottle, in



Fig. 28.



Fig. 29.

which is fitted a cork with two holes (see Fig. 28), or in a bottle with two necks called a Wolff's flask (see Fig. 29). Through one of the holes a funnel-tube passes, and through the other a glass tube bent in a convenient form.

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* If it is desired to dilute ordinary concentrated sulphuric acid with water, the acid should be poured slowly into the water while the mixture is constantly stirred. If the water is poured into the acid, the heat evolved at the places where the two come in contact may be so great as to convert the water into steam and cause the strong acid to spatter.

The zinc used is granulated. It is prepared by melting it in a ladle, and pouring the molten metal from an elevation of four or five feet into water. The advantage of this form is that it presents a large surface to the action of the acids. A handful of this zinc is introduced into the bottle, and enough of a *cooled* mixture of sulphuric acid and water (1 volume concentrated acid to 6 volumes water) poured upon it to cover it. Usually a brisk evolution of gas takes place at once. Wait for two or three minutes, and then collect some of the gas by displacement of water. When the action becomes slow, add more of the dilute acid. It will be well to fill several cylinders and bottles with the gas, and also a gasometer, from which it can be taken as it is needed for experiments.

### Something besides Hydrogen is formed.
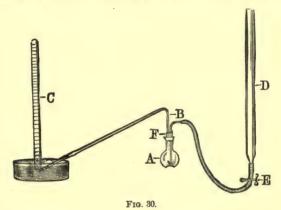
**Experiment 34.**—After the action is over pour the contents of the flask through a filter into an evaporating-dish, and boil off the greater part of the water, so that, on cooling, the substance contained in solution will be deposited. If the operation is carried on properly, the substance will be deposited in regular forms called crystals. It is zinc sulphate, $ZnSO_4$, formed by the replacement of the hydrogen of the sulphuric acid by zinc.

PROBLEMS.—How much zinc would it take to give 200 liters of hydrogen? How much zinc sulphate would be formed? How much hydrogen would be formed by the action of 50 grams of zinc on sulphuric acid? How much sulphuric acid would be used up?

### Determination of the Amount of Hydrogen evolved when a Known Weight of Zinc is dissolved in Sulphuric Acid.

**Experiment 35.**—This determination can be made by means of an apparatus such as represented in Fig. 30. The bent tube leading from the flask $A$ is drawn out at $B$, and a plug of glass-wool introduced below the constriction. The other parts of the apparatus need no description. The flask should have a capacity of about 40 to 50 cc.; and the measuring tube $C$ should have a capacity of about 100 cc., and be graduated to $\frac{1}{10}$ cc.

"The experiment is conducted in the following manner: *D* is filled with distilled water; a piece of zinc weighing from 0.150 to 0.200 gram is placed in the flask; the pinch-cock *E* is then opened, and the whole apparatus thus filled with water. The apparatus is now examined in order to ascertain if gas bubbles are lodged under the stopper *F* or in the glass-wool. If so, they can usually be dislodged without difficulty. If they persist, a few moments' boiling of the water in the flask will effect their complete removal. . . The eudiometer is now placed over the outlet of the delivery-tube, and the greater portion of the water remaining in *D* allowed to flow through the apparatus. Sulphuric acid of the concentration ordinarily employed in the laboratory (1 of $H_2SO_4$ to 4 of $H_2O$) is poured into the reservoir *D* until it is nearly full. The pinch-cock *E* is then opened, and the water which fills the



FIG. 30.

apparatus is displaced by sulphuric acid. The action of the acid upon the metal may be facilitated by heat or by adding some platinum scraps. When the action is over, the contents of the flask are swept through the delivery-tube by again opening the pinch-cock *E*. Finally, the measuring-tube is transferred to a cylinder of water, and the volume of the gas read and corrected in the usual manner. If hydrochloric instead of sulphuric acid has been used, which would be the case when the metal employed is aluminium, a little caustic soda should be added to the water in the cylinder to which the eudiometer is transferred." *

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* See Morse and Keiser, *American Chemical Journal*, vol. vi. p. 349.

A liter of hydrogen at 0° and 760 mm. weighs 0.089873 gram.   How much does the hydrogen obtained in the experiment weigh?   How much ought to have been obtained? How many cubic centimeters of hydrogen ought to have been obtained?

Try the same experiment, using tin and hydrochloric acid. The action takes place as represented in the equation

$$Sn + 2HCl = SnCl_2 + H_2.$$

It would be well, further, to try the experiment also with iron and sulphuric acid, and with aluminium and hydrochloric acid, and to calculate from the results the relation between the weights of the four metals required to give equal volumes of hydrogen, and the volumes of hydrogen given by, say, a gram of each metal.   The action between iron and sulphuric acid takes place according to the equation

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

That between aluminium and hydrochloric acid is represented by this equation :

$$Al + 3HCl = AlCl_3 + 3H.$$

## HYDROGEN IS PURIFIED BY PASSING THROUGH A SOLUTION OF POTASSIUM PERMANGANATE.

**Experiment 36.**—Pass some of the gas, made by the action of zinc on sulphuric acid, through a wash cylinder contain-
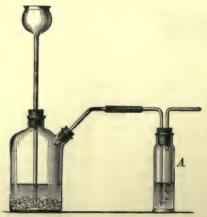


Fig. 31.

ing a solution of *potassium permanganate;* collect some of it, and notice whether it has an odor.   The apparatus should

be arranged as shown in Fig. 31. The solution of potassium permanganate is, of course, contained in the small cylinder *A*, and the tubes so arranged that the gas bubbles through it.

Has the gas any odor or taste or color?

**Experiment 37.**—Place a vessel containing hydrogen with the mouth upward and uncovered. In a short time examine the gas contained in the vessel, and see whether it is hydrogen. What does this experiment prove with reference to the weight of hydrogen as compared with that of the air?

**Experiment 38.**—Gradually bring a vessel containing hydrogen with its mouth upward below an inverted vessel containing air, in the way shown in Fig. 32. After the vessel which contained the hydrogen has been brought in the upright position beneath the other, examine the gas in each vessel. Which one contains the hydrogen?



Fig. 32.

**Experiment 39.**—Soap-bubbles filled with hydrogen rise in the air. This experiment is best performed by connecting an ordinary clay pipe by means of a piece of rubber tubing with the delivery-tube of a gasometer filled with hydrogen. Small balloons of collodion are also made for the purpose of showing the lightness of hydrogen.

HYDROGEN PASSES READILY THROUGH POROUS VESSELS. DIFFUSION.

**Experiment 40.**—Arrange an apparatus as shown in Fig. 33. It consists of a porous earthenware cup, such as is used in galvanic batteries, fitted with a perforated cork connected with a glass tube 2 to 3 feet long. The cork must fit air-tight into the mouth of the cup, as well as the tube into the cork. This may be secured by shoving the cork into the cup until its outer surface is even with the edge of the cup, and then covering it carefully with sealing-wax. Put the lower end of the glass tube through a cork into one neck of a Wolff's bottle containing some water colored with litmus or indigo, so that the end of the tube is above the surface of the water. Through the other neck of the bottle pass a tube slightly bent outward and drawn out at the end to a fine opening. This

tube must also be fitted to the bottle by an air-tight cork, and its lower end must be below the surface of the liquid. Now bring a bell-jar containing dry hydrogen over the porous cup, when the liquid will be seen to rise in the short, bent tube that dips below the liquid, and be forced out of it, sometimes with considerable velocity. Withdraw the bell-jar, and bubbles will rise rapidly from the bottom of the tube which dips under the water, thus showing that air is enter-

FIG. 33.

FIG. 34.

ing the bottle. This is due to the diffusion of the hydrogen from the porous cup into the air. Explain all that you have seen.

### CHEMICAL PROPERTIES OF HYDROGEN.

**Experiment 41.**—If there is no small platinum tube available, roll up a small piece of platinum-foil and melt it into the end of a glass tube, as shown in Fig. 34. Connect the burner thus made with the gasometer containing hydrogen, and after the gas has been allowed to issue from it for a moment, set fire to it. In a short time it will be seen that the flame is practically colorless, and gives no light. That it is

hot can be readily shown by holding a piece of platinum wire or a piece of some other metal in it.

**Experiment 42.**—Into the flame of burning hydrogen introduce a small coil of platinum wire. What change is observed? Introduce also a piece of magnesium ribbon. Explain the difference between the two cases. What becomes of the magnesium? of the platinum?

**Experiment 43.**—Hold a cylinder filled with hydrogen with the mouth downward. Insert into it a lighted taper held on a bent wire, as shown in Fig. 35. The gas takes fire at the mouth of the vessel, but the taper is extinguished. On withdrawing the taper and holding the wick for a moment in the burning hydrogen, it will take fire, but on putting it back in the hydrogen it will again be extinguished. Other burning substances should be tried in a similar way. What conclusions are justified by the last two experiments?
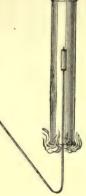


Fig. 35.

## PRODUCT FORMED WHEN HYDROGEN IS BURNED.

**Experiment 44.**—Hold a clean, dry glass plate a few inches above a hydrogen flame. What do you observe? Remove what is deposited upon the plate, and hold the plate again over the flame. Repeat this a number of times. What does the substance deposited upon the plate suggest? Can you positively say what it is?

## REDUCTION.

**Experiment 45.**—Arrange an apparatus as shown in Fig. 36. The flask *A* contains zinc and dilute sulphuric acid; the cylinder *B* a solution of potassium permanganate; the cylinder *C* concentrated sulphuric acid; and the tube *D* granulated calcium chloride. The object of the potassium permanganate is to purify the hydrogen; the object of the concentrated sulphuric acid and calcium chloride is to remove moisture from the gas. In the tube *E* put a few pieces of the black oxide of copper, or cupric oxide, $CuO$. After hydrogen has been passing long enough to drive all the air out of the apparatus (about two or three minutes if there is a brisk evolution) heat

the oxide of copper by means of a flame applied to the tube. What change in color takes place? Try the action of nitric
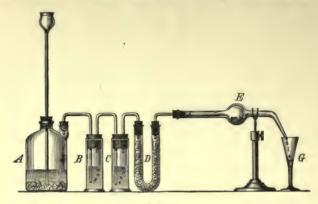


FIG. 36.

acid on the substance before the action and after, and note whether there is any difference. What appears in $G$? Explain what you have seen.

**Experiment 46.**—Try the experiment just described, using ferric oxide, or oxide of iron, $Fe_2O_3$, instead of cupric oxide. What is the common feature in the two reactions?

### EXPERIMENTS TO ACCOMPANY CHAPTER IV.

#### COMPOSITION OF WATER.

**Experiment 47.**—Arrange the apparatus shown in Fig. 36 with a straight tube instead of the bent tube $E$, and connect this with a small bent tube containing calcium chloride, as shown in Fig. 37. Weigh tube $E$ empty, and after the cupric



FIG. 37.

oxide has been put into it. This gives the weight of the cupric oxide. Weigh the tube $F$ before the experiment. Now proceed as in Experiment 45. In this case all the water formed by the action of the hydrogen on the cupric oxide will be

absorbed by the calcium chloride in tube *F*. This tube will therefore gain in weight, and as oxygen is removed from the cupric oxide, tube *E* will lose in weight. After the reduction is complete weigh tube *E* and tube *F* again.

Let *x* = weight of tube *E* + cupric oxide before the experiment;
*y* = weight of tube *E* + copper after the experiment.
Then *x* − *y* = weight of oxygen removed from the cupric oxide.
Let *a* = weight of tube *F* before the experiment,
and *b* = " " " after " "
Then *b* − *a* = weight of water formed.

If the experiment is properly performed, it will be found that the ratio $\frac{x-y}{b-a}$ is very nearly $\frac{8}{9}$. Or the result may be stated thus: In nine parts of water there are eight parts of oxygen.

**Experiment 48.**—The tubes in the apparatus used in Experiment 3, or some other similar apparatus, should be graduated. Let the gases formed by the action of the electric current, as in Experiment 3, rise in the tubes, and observe the volumes. It will be seen that when one tube is just full of gas, the other, if it is of the same size, will be only half full. On examining the gases the larger volume will be found to be hydrogen, and the smaller volume oxygen. What are the relative weights of equal volumes of hydrogen and oxygen? In what proportion by weight are the two gases obtained from water in this experiment? How does this result agree with that obtained in the preceding experiment? Does this experiment prove that water consists only of hydrogen and oxygen?

**Experiment 49.**—Pass hydrogen from a generating-flask or a gasometer through a tube containing some substance that will absorb moisture ; for all gases made in the ordinary way and collected over water are charged with moisture. The calcium chloride should be in granulated form, not powdered. After passing the hydrogen through the calcium chloride, pass it through a tube ending in a narrow opening, and set fire to it. If now a *dry* vessel is held over the flame, drops of water will condense on its surface and run

**down.** A convenient arrangement of the apparatus is shown in Fig. 38.
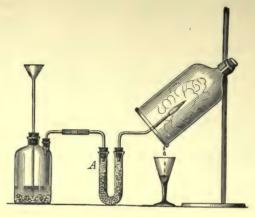
*A* is the calcium chloride tube. Before lighting the jet, hold a glass plate in the escaping gas, and see whether water is deposited on it. Light the jet *before* putting it under the bell-jar; otherwise, if hydrogen is allowed to escape into the vessel, it will contain a mixture of air and hydrogen, and this mixture, as we shall soon see, is explosive.

**Experiment 50.**—Mix hydrogen and oxygen in the proportions of about 2 volumes of hydrogen to 1 volume of oxygen, in a gasometer. Fill soap-bubbles, made as directed in Experiment 39, with this mixture, and allow them to rise in the air. As they rise, bring a lighted taper in contact with them, when a sharp explosion will occur. Great care must be taken to keep all flames away from the vicinity of the gasometer while the mixture is in it. This experiment is conveniently performed by hanging up, about six to eight feet above the experiment-table, a good-sized tin funnel-shaped vessel, with the mouth downward. Now place a gas jet or a small flame of any kind at the mouth of the vessel. If the soap-bubbles are allowed to rise below this apparatus they will come in contact with the flame and explode at once.* What does this experiment show? Does it give any information in regard to the composition of water?    .

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* The same apparatus may be used in experimenting with soap-bubbles filled with hydrogen.

## EUDIOMETRIC EXPERIMENTS.

**Experiment 51.**—The general method of studying the combination of hydrogen and oxygen by means of the eudiometer was described in the text (see p. 50). To what was there said it need only be added that, in exploding the mixture in the eudiometer, the latter should be held down firmly, by means of a clamp, against a thick piece of rubber cloth placed on the bottom of the mercury-trough. In making the measurements of the volume of the gases and the height of the mercury column, care must be taken to have the eudiometer in a perpendicular position. This can be secured by means of plumb-lines suspended from the ceiling and reaching nearly to the table, by which the position of the eudiometer can be adjusted.

### OXYHYDROGEN BLOW-PIPE.

**Experiment 52.**—Hold in the flame of the oxyhydrogen blow-pipe successively a piece of iron wire, a piece of a steel watch-spring, a piece of copper wire, a piece of zinc, a piece of platinum wire.

**Experiment 53.**—Cut a piece of lime of convenient size and shape, say an inch long by three quarters of an inch wide, and the same thickness. Fix it in position so that the flame of the oxyhydrogen blow-pipe will play upon it. The light is very bright, but by no means as intense as the electric light.

### EXPERIMENTS TO ACCOMPANY CHAPTER V.

### ORGANIC SUBSTANCES CONTAIN WATER.

**Experiment 54.**—In dry test-tubes heat gently various organic substances as a piece of wood, fresh meat, fruits, vegetables, etc.

### WATER OF CRYSTALLIZATION.

**Experiment 55.**—Take some of the crystals of zinc sulphate obtained in Experiment 34. Spread them out on a layer of filter-paper, and finally press two or three of them between folds of the paper. Examine them carefully. They appear to be quite dry, and in the ordinary sense they are dry. Heat them in a dry tube, when it will be observed that water condenses in the upper part of the tube, while the

crystals lose their lustre, becoming white and opaque, and at last crumbling to powder.

**Experiment 56.**—Perform a similar experiment with some gypsum, which is the natural substance from which "plaster of Paris" is made.

**Experiment 57.**—Heat a few small crystals of copper sulphate, or blue vitriol. In this case the loss of water is accompanied by a loss of color. After all the water is driven off, the powder left behind is white. On dissolving it in water, however, the solution will be seen to be blue ; and if the solution is evaporated until the substance is deposited, it will again appear in the form of blue crystals.

### EFFLORESCENT SALTS.

**Experiment 58.**—Select a few crystals of sodium sulphate which have not lost their lustre. Put them on a watch-glass, and let them lie exposed to the air for an hour or two. They soon lose their lustre, and undergo the changes noticed in heating zinc sulphate.

### DELIQUESCENT SALTS.

**Experiment 59.**—Expose a few pieces of calcium chloride to the air. Its surface will soon give evidence of the presence of moisture, and after a time the substance will dissolve in the water which is absorbed.

### PURIFICATION OF WATER BY DISTILLATION.

**Experiment 60.**—In an apparatus like that shown in Fig. 39 distil a dilute solution of copper sulphate or some other
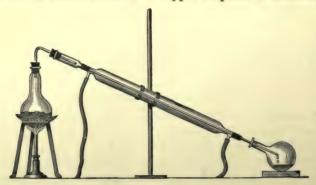


FIG. 39.

colored substance. A slow current of cold water must be

kept running through the condenser by connecting the lower rubber tube with a water-cock. When the water is boiled in the large flask, the steam passes into the inner tube of the condenser. As this is surrounded by cold water, the steam condenses and the distilled water collects in the receiver.

## EXPERIMENTS TO ACCOMPANY CHAPTER VI.

It would be well in this connection to determine the specific gravity of some substance in the form of vapor. The principal methods for this purpose are those of Dumas, Gay Lussac, Hofmann, and Victor Meyer. That of Dumas, which consists in measuring the volume and determining the weight of the vapor under observation, is the most accurate. The method of Hofmann is a modification of that of Gay Lussac. It consists in weighing a small quantity of the liquid the specific gravity of whose vapor is to be determined, and, after introducing the liquid in a minute glass vessel into a eudiometer over mercury, heating the eudiometer and its contents by passing steam through a jacket surrounding it and measuring the volume of vapor formed. The method of Victor Meyer is used very commonly, especially when it is required to determine the specific gravity of the vapor of a substance which boils at a high temperature.

## METHOD OF DUMAS.

**Experiment 61.**—In this method the liquid to be vaporized is brought into a small balloon like that shown in Fig. 40. The dry balloon is first weighed, and a small quantity of liquid then introduced by gently heating the balloon and putting the point of its stem into the liquid, when, on cooling, the liquid rises and enough is easily brought into the balloon in this way. The balloon is now placed (in the position shown in Fig. 41) in a bath of water, oil, or paraffin, according to the boiling-point of the liquid. The bath is heated 30–40° above the boiling-point of the liquid under examination. The air is thus driven out and the balloon is filled with the vapor. When vapor no longer escapes, the point of the stem is closed by melting it with a mouth blow-pipe. The balloon is then cleaned, dried, and weighed. The temperature of the bath and the height of the barometer are observed at the time the balloon is closed. The point of the stem is broken off under

mercury, when the mercury rises and fills the balloon. By pouring the mercury out into a graduated cylinder the capacity of the balloon is determined. The specific gravity of the vapor is calculated by the aid of the formula

$$D = \frac{760(B_, - B + p)(1 + 0.00366 \times t_,)}{vh_, \times 0.001293},$$

**in** which

$B$ = weight of balloon at $t°$ and $h$ mm.;
$B_, =$ " " " with vapor, at $t_,°$ and $h_,$ mm.;
$v$ = capacity of the balloon in cubic centimeters;
**0.001293** = weight of 1 cc. air at $0°$ and 760 mm.;
$p$ = weight of air in balloon at $t°$ and $h$ mm.



FIG. 40.            FIG. 41.

METHOD OF VICTOR MEYER.

**Experiment 62.**—In this method a known weight of substance is converted into vapor, and the volume of vapor formed is determined by measuring the volume of air which it displaces. The apparatus consists of an outer cylindrical vessel $A$, Fig. 42, and an inner vessel $B$, which is connected with a tube $C$. The vessel $B$ has a capacity of about 100 cc., and is about 200 mm. long. The tube $C$, with its funnel-shaped end $E$, is about 600 mm. long. First, a small quantity of some substance with a boiling-point high enough to secure the complete conversion into vapor of the substance to be studied, is put in the bottom of the vessel $A$, and a little ignited asbestos or dry

mercury in the bottom of the vessel $B$. The substance in $A$ is now heated to boiling, and $E$ is closed with a rubber stopper. After a time the temperature of the air in $B$ is raised to that of the vapor in $A$, and no more escapes from the tube $D$. When this condition of equilibrium is reached, a small weighed quantity of the substance under examination is dropped into the vessel $B$, the stopper being removed from $E$ and quickly replaced. The substance is converted into vapor, and displaces an equivalent volume of air, and this displaced air is collected over water in the measuring-tube placed over the end of $D$. When no more air escapes, the volume is determined in the usual way. The specific gravity of the substance is calculated by the aid of the following formula:

$$D = S \cdot \frac{(1 + 0.00366 \times t)760}{(B - w)\,V \times 0.001293},$$

in which 0.001293 is the weight of 1 cc. air in grams at 760 mm. and 0°; and, further,

$S =$ weight of substance taken;
$t =$ temperature of the room, or of the water in the measuring apparatus;
$B =$ height of barometer;
$w =$ tension of aqueous vapor;
$V =$ observed volume of air;

or, the formula can be simplified by division, when it takes this form:

$$D = S\frac{(1 + 0.00366 \times t)587,780}{(B - w)\,V}.$$

The above is the simplest form of apparatus used. To avoid opening and shutting the vessel in order to introduce the substance, an arrangement has been devised for holding the substance below the stopper until the proper temperature is reached, and then releasing it without disturbing the stopper.

### EXPERIMENTS TO ACCOMPANY CHAPTER VII.

#### OZONE.

**Experiment 63.**—Put a few sticks of ordinary phosphorus on the bottom of a good-sized bottle with a wide mouth, and

partly cover the phosphorus with water. In a short time the odor of ozone will be perceptible, and the gas can also be detected by means of strips of paper which have been moistened with a dilute solution of potassium iodide and starch-paste. See whether such papers are changed in the air? What is the cause of the change? If convenient, examine the air in the neighborhood of a frictional electrical machine, and see whether it causes the papers to change color.

## HYDROGEN DIOXIDE.

**Experiment 64.**—Finely powder some barium dioxide, and add some of it to dilute sulphuric acid. Filter from the precipitated barium sulphate, and with the solution try the following reactions :

Heat some in a test-tube. What takes place?—Add to another small portion a little of a dilute solution of potassium permanganate. To another portion add a little finely powdered manganese dioxide. What is given off?—To a dilute solution contained in a small stoppered cylinder add a few drops of a dilute solution of potassium dichromate, and quickly add ether, and shake the cylinder thoroughly.

## EXPERIMENTS TO ACCOMPANY CHAPTER VIII.

### PREPARATION OF CHLORINE.

**Experiment 65.**—Pour 2 or 3 cc. concentrated sulphuric acid on a gram or two of common salt in a test-tube. A gas will be given off which forms dense white fumes in the air and has a sharp, penetrating taste and smell. This is hydrochloric acid gas.

**Experiment 66.**—Pour 2 or 3 cc. concentrated sulphuric acid on a few grams of manganese dioxide in a test-tube. Heat, and examine the gas given off. Convince yourself that it is oxygen.

**Experiment 67.**—Mix 2 grams manganese dioxide and 2 grams common salt. Pour 4 to 5 cc. dilute sulphuric acid on the mixture in a test-tube. This experiment should be performed under a hood in which the draught is good, as the gas which is given off is not only disagreeable, but irritating to the respiratory organs. Notice the color and odor of the gas. [Does it support combustion? Does it burn?]

The best way to make chlorine is the following : Mix 5 parts coarsely granulated manganese dioxide and 5 parts coarse-ly granulated common salt. Make a mixture of 12 parts concentrated sulphuric acid and 6 parts water. Let this mixture cool down to the tem-perature of the room, and then pour it upon the mixture of salt and manganese dioxide. Gently heat on a sand-bath, and a regular current of chlo-rine will be given off. The gas is collected by displacement of air in a dry glass vessel. The apparatus for the purpose is arranged as shown in Fig. 43. The delivery-tube should reach



Fig. 43.

to the bottom of the collecting vessel, and the mouth of the vessel should be covered with a piece of paper to prevent cur-rents of air from carrying away the chlorine. As the gas col-lects in the vessel the experimenter can judge of the quantity present by means of the color.

**Experiment 68.**—Collect six or eight dry cylinders or bot-tles full of chlorine. Make the gas from about 30 grams of manganese dioxide, using the other substances in the propor-tions already stated.

(1) Introduce into one of the vessels containing chlorine a little finely powdered antimony.

(2) Into a second vessel put a few pieces of heated thin copper-foil.

(3) Into a third vessel put a piece of paper with some writ-ing on it, some flowers, and pieces of cotton print. The sub-stances used must be moist.

(4) Into a fourth vessel put a dry piece of the same cotton print as that used in the previous experiment.
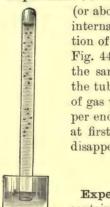
What conclusions do the results of the above experiments justify as to the conduct of chlorine?

**Experiment 69.**—Cut a piece of filter-paper about an inch wide and six to eight inches long. Pour on this some ordinary oil of turpentine previously warmed slightly. Introduce this into one of the vessels of chlorine. A flash of flame is noticed,

and a dense black cloud is formed. The action in this case is due to the great affinity of chlorine for hydrogen. Oil of turpentine consists of carbon and hydrogen. The main action of the chlorine consists in extracting the hydrogen and leaving the carbon. The experiment is interesting chiefly in so far as it illustrates the general tendency of chlorine to act upon vegetable substances.

### Chlorine decomposes Water in the Sunlight.

**Experiment 70.**—Seal the end of a glass tube about a metre (or about a yard) long and about 12 mm. ($\frac{1}{2}$ inch) internal diameter. Fill this with a strong solution of chlorine in water. Invert it as shown in Fig. 44, in a shallow vessel containing some of the same solution of chlorine in water. Place the tube in direct sunlight. Gradually bubbles of gas will be seen to rise and collect in the upper end, and the color of the solution, which is at first greenish yellow, like that of chlorine, disappears. The gas can be shown to be oxygen.

### Chlorine Hydrate.

**Experiment 71.**—Conduct chlorine into a flask containing water cooled down to about 2° or 3° Centigrade. If crystals are formed remove some by filtering out-of-doors if the weather is cold. Expose some of the crystals on filter-paper under a hood in the laboratory. What changes have taken place?

FIG. 44.
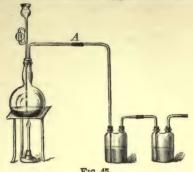
### Formation of Hydrochloric Acid.

**Experiment 72.**—Light a jet of hydrogen in the air and carefully introduce it into a vessel containing chlorine. It will continue to burn, but the flame will not appear the same. A gas will be given off which forms clouds in the air. This gas has a sharp, penetrating taste and smell.

**Experiment 73.**—Half fill a small, wide-mouthed cylinder over hot water with chlorine gas. Then fill it with hydrogen. The direct sunlight must not shine upon the cylinder while it contains the mixture. Turn it mouth upward and apply a flame.

## PREPARATION OF HYDROCHLORIC ACID.

**Experiment 74.**—Arrange an apparatus as shown in Fig. 45.



FIG. 45.

Weigh out 5 parts common salt, 5 parts concentrated sulphuric acid, and 1 part water. Mix the acid and water, taking the usual precautions; let the mixture cool down to the ordinary temperature, and then pour it on the salt in the flask. For the purposes of the experiment take about 20 grams of salt. Now heat the flask gently, and the gas will be regularly evolved. Conduct it at first through water contained in the two Wolff's bottles until what passes over is all absorbed in the first bottle. The reason why gas at first bubbles through all the bottles is, that the apparatus is full of air, which is first driven out. When the air has been displaced, the gas is all absorbed as soon as it comes in contact with the water.—After the gas has passed for ten to fifteen minutes, disconnect at *A*. Notice the fumes. These become denser by blowing the breath on them. Why?—Apply a lighted match to the end of the tube. Does the gas burn? —Collect some of the gas in a dry cylinder by displacement of air, as in the case of chlorine. The specific gravity of the gas being 1.26, the vessel must of course be placed with the mouth upward. That the gas is colorless and transparent is shown by the appearance of the generating flask, which is filled with the gas. Insert a burning stick or candle in the cylinder filled with the gas.—Reconnect the generating-flask with the series of bottles containing water, and let the process continue until no more gas comes over. The reaction represented in the equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

is now complete. Disconnect the flask, and after it has cooled down pour water on the contents ; when the substance is dissolved filter it and evaporate to such a concentration that, on cooling, the sodium sulphate is deposited. Pour off the liquid and dry the solid substance by means of filter-paper. Compare the substance with the common salt which you put in the flask before the experiment. What proofs have you that the two substances are not the same?—Heat a small piece of each in a dry tube closed at one end. What differences do you notice?—Treat a small piece of each in a test-tube with sulphuric acid. What difference do you notice?—If in the experiment we should recover all the sodium sulphate formed, how much should we have?—Put about 50 cc. of the liquid from the first Wolff's bottle in a porcelain evaporating-dish. Heat over a small flame just to boiling. Is hydrochloric acid given off? Can all the liquid be driven off by boiling?—Try the action of the solution on some iron filings. What is given off?—Add some to a little granulated zinc in a test-tube. What is given off?—Add a little to some manganese dioxide in a test-tube. What is given off? —Add ten or twelve drops of the acid to 2 to 3 cc. water in a test-tube. Taste the dilute solution. It has what is called a *sour* or *acid taste*, the two terms being practically synonymous.—Add a drop or two of a solution of *blue* litmus, or put into it a piece of paper colored *blue* with litmus. What change takes place? Litmus is a vegetable color prepared for use as a dye. Other vegetable colors are changed by hydrochloric acid.—Steep a few leaves of red cabbage in water. Add a few drops of the solution thus obtained to dilute hydrochloric acid. Is there any change in color?—The color will be restored in each case by adding a few drops of a solution of caustic soda.—In what experiment has caustic soda been obtained? What relation does it bear to water?— To the dilute solution of hydrochloric acid add drop by drop a dilute solution of caustic soda. Is the acid taste destroyed?

## EXPERIMENTS TO ACCOMPANY CHAPTER IX.

### CHLORIC ACID AND POTASSIUM CHLORATE.

**Experiment 75.**—Dissolve 40 grams (or about 1¼ ounces) caustic potash in 100 cc. water in a beaker-glass, and pass chlorine into it. When chlorine passes freely through the

solution, thus indicating that it is no longer absorbed, stop the action. After boiling filter the solution and allow it to cool, when crystals of potassium chlorate will be deposited, mixed with a little potassium chloride. Recrystallize from a little water. Filter off the crystals and dry them. What evidence have you that the substance is potassium chlorate? Does it give off oxygen when heated? In a dry test-tube pour two or three drops of concentrated sulphuric acid on a *small* crystal of the substance. Do the same with a piece of potassium chlorate from the laboratory bottle. Hold the mouth of the test-tube away from the face. What is noticed in each case? —Evaporate the solution from which the crystals of potassium chlorate have been removed. On allowing it to cool crystals will again be deposited. Take them out and recrystallize them. Does this substance give off oxygen when heated? Does it give off a gas when treated with sulphuric acid? Is this gas colored? Is it hydrochloric acid? How do you know that it is? If the gas is hydrochloric acid, what is the solid substance from which it is formed? And what is left in the test-tube?

**Experiment 76.**—Mix 10 grams fresh quick-lime with 20 cc. water. After the slaking is over, pass chlorine into it until the gas is no longer absorbed. Put the powder thus formed in a flask arranged as shown in Fig. 46. Pour a mixture of equal parts of sulphuric acid and water slowly through the funnel-tube. Collect by displacement of air the gas given off. What evidence have you that the gas is chlorine?
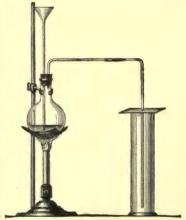


Fɪɢ. 46.

## Perchloric Acid.

**Experiment 77.**—Make potassium perchlorate as follows: Gently heat 50 to 100 grams potassium chlorate until after having been liquid it becomes thick and pasty, and gas is not given off without raising the temperature. After cooling, break up the mass and treat it with cold water. This dissolves

out the potassium chloride and leaves the perchlorate, which can then be crystallized from hot water. After the crystallized salt is dried it is decomposed by sulphuric acid. To effect this decomposition, the finely powdered salt (10 parts) is treated in a retort with 20 parts of pure sulphuric acid which is free from nitric acid and diluted with $\frac{1}{10}$ its volume of water. The retort is connected with a receiver which can be well cooled. The mixture is heated, and when the perchloric acid begins to come over, the heat is so regulated that the temperature does not rise above 140°. When the mixture has become colorless the operation is ended.

## EXPERIMENTS TO ACCOMPANY CHAPTER X.

### NEUTRALIZATION OF ACIDS AND BASES; FORMATION OF SALTS.

**Experiment 78.**—Make dilute solutions of nitric, hydrochloric, and sulphuric acids (1 part dilute acid, such as is used
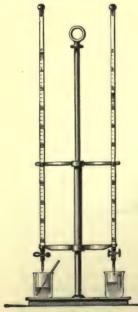


FIG. 47.

in the laboratory, to 50 parts water), and of caustic soda and caustic potash (about 1 gram to 200 cc. of water). Measure off about 20 cc. of one of the acid solutions. Add a few drops of a solution of blue litmus. Gradually add to the measured quantity of acid sufficient dilute caustic soda to cause the red color just to change to blue. As long as the solution is red it is acid. When it turns blue it is alkaline. At the turning-point it is neutral. The operation is best carried on by means of a burette, which is a graduated tube with an opening from which small quantities can be poured. A convenient shape is that represented in Fig. 47. At the lower end is a small opening. The flow of the liquid from the burette is controlled by means of a small pinch-cock. It will require some practice to enable the student to know ex-

actly when the red color disappears and the blue appears, but with practice the point can be discerned with great accuracy. Should too much alkali be allowed to get into the acid, add a small measured quantity of the acid from another burette. Having in one experiment determined how much of the solution of alkali is required to cause the red color to change to blue in operating on a given quantity of the acid solution, try the experiment again, using a different quantity of the acid solution. If the results of several experiments with the same acid and alkali are recorded, it will be found that there is a definite ratio between the quantities of acid and alkali solution required to neutralize one another. If, for example, 15 cc. of the alkali solution are required to neutralize 20 cc. of the acid solution, 18 cc. of the alkali solution will be required to neutralize 24 cc. of the acid solution, 30 cc. to neutralize 40 cc., etc. In other words, in order to neutralize a given quantity of an acid, a definite quantity of an alkali is necessary. Perform similar experiments with the other acids. Afterwards carefully examine the numerical results. Suppose it should require 15 cc. of the caustic-soda solution or 12 cc. of the caustic-potash solution to neutralize 20 cc. of the hydrochloric-acid solution. Compare the quantities of these alkali solutions necessary to neutralize equal quantities of the other acids. What conclusion is justified with reference to the act of neutralization?

## STUDY OF THE PRODUCTS FORMED.

**Experiment 79.**— Dissolve about 10 grams caustic soda in 100 cc. water. Add hydrochloric acid slowly, examining the solution from time to time by means of a piece of paper colored blue with litmus. As long as the solution is alkaline it will cause no change in the color of the paper. The instant the point of neutralization is passed, the solution changes the color of the paper to red; when exactly neutral, it will neither change the blue to red, nor, if the color is changed to red by means of another acid, will it change it back again. When this point is reached, evaporate to complete dryness on the water-bath, and see what is left. Taste the substance. Has it an acid taste? Does it suggest any familiar substance? If it is sodium chloride, how ought it to conduct itself when treated with sulphuric acid? Does it conduct itself in this way? Satisfactory evidence can be given that the substance

is sodium chloride. It is not an acid nor an alkali. It is neutral.

**Experiment 80.**—Perform a similar experiment, using dilute nitric acid and caustic soda. What evidence have you that the product in this case is different from caustic soda?

**Experiment 81.**—Perform similar experiments with dilute sulphuric acid and caustic soda; with sulphuric acid and caustic potash; with nitric acid and caustic potash; with hydrochloric acid and caustic potash. Dry and examine the product carefully in each case; and keep for future study what is not used in these experiments.

### FOR CHAPTER XI.

A large table of the Natural System of the Elements, like that on page 151, should be hung up in a conspicuous place in the laboratory. It would be well also to have such a table pasted upon a cylinder which can be revolved on its axis, so that the continuity of the system may be impressed upon the mind.

### EXPERIMENTS TO ACCOMPANY CHAPTER XII.

#### PREPARATION OF BROMINE.
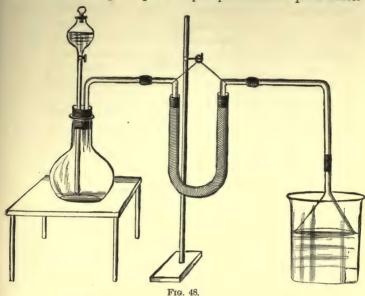
**Experiment 82.**—Mix together 3.5 grams potassium bromide and 7 grams manganese dioxide. Put the mixture into a 500 cc. flask; connect with a condenser (see Fig. 39). Mix 15 cc. concentrated sulphuric acid and 90 cc. water. After cooling pour the liquid on the mixture in the flask. Gently heat, when bromine will be given off in the form of vapor. A part of this will condense and collect in the receiver. Perform this experiment under a hood with a good draught.

#### HYDROBROMIC ACID.

**Experiment 83.**—In a small porcelain evaporating-dish put a few crystals of potassium bromide. Pour on them a few drops of concentrated sulphuric acid. The white fumes of hydrobromic acid and the reddish-brown vapor of bromine are noticed. Treat a few crystals of potassium or sodium chloride in the same way. What difference is there between the two cases?

The preparation of hydrobromic acid may be shown in the lecture-room as follows:

**Experiment 84.**—Arrange an apparatus as shown in Fig. 48. In the flask put 1 part red phosphorus and 2 parts water.



FIG. 48.

Let 10 parts bromine gradually drop into the flask from the glass-stoppered funnel. Pass the gas through a U-tube loosely packed with asbestos containing red phosphorus in order to free the hydrobromic acid from bromine, which to some extent passes over with it. Collect some of the gas in water, and examine the solution. How does the gas act when allowed to escape in the air? Fill a cylinder with the gas in the same way as was done with hydrochloric acid, and fill another with chlorine. While covered with glass plates bring their mouths together. Then withdraw the plates. What change is observed? What is this due to?

**Experiment 85.**—To a dilute solution of sodium hydroxide add bromine water made by shaking up a little liquid bromine in a bottle with water. What change takes place? Add sulphuric acid until the liquid shows an acid reaction. What takes place? The changes here referred to are perfectly analogous to those which would take place if chlorine were used instead of bromine. Shake a solution containing a little free bromine with ether; with chloroform; with carbon disulphide. What changes do you observe?

## Iodine.

**Experiment 86.**—Mix about 2 grams of sodium or potassium iodide and 4 grams manganese dioxide. Treat with a little concentrated sulphuric acid in a one to two liter flask. Heat gently on a sand-bath. Gradually the vessel will be filled with the beautiful colored vapor of iodine. In the upper parts of the flask some of the iodine will be deposited in the form of crystals of a grayish-black color.

**Experiment 87.**—Make solutions of iodine in water, in alcohol, and in a water solution of potassium iodide. Use small quantities in test-tubes.

**Experiment 88.**—Dissolve a piece of potassium iodide the size of a small pea in about 100 cc. water in a stoppered cylinder. Add enough carbon disulphide to make a layer about an inch thick at the bottom of the cylinder. Shake the two liquids together. Does the carbon disulphide become colored? Add a drop of chlorine water and shake again. What difference do you observe in the two cases? Explain this. Try the same experiment, using chloroform instead of carbon disulphide.

### Iodine can be detected by Means of its Action upon Starch-paste.

**Experiment 89.**—Make some starch-paste by covering a few grains of starch in a porcelain evaporating-dish with cold water, grinding this to a paste, and pouring 200–300 cc. boiling-hot water on it. After cooling add a little of this paste to a dilute water solution of iodine. The solution will turn blue if the conditions are right. Now add a little of the paste to a diluted water solution of potassium iodide. Is there any change? Add a drop or two of a solution of chlorine in water. Why the difference? Will not chlorine water alone act this way toward starch-paste?

### Action of Sulphuric Acid upon Potassium Iodide.

**Experiment 90.**—Bring a piece of potassium iodide the size of a pea in a dry test-tube ; add *one* drop of water and three or four drops of concentrated sulphuric acid ; the salt becomes brown ; heat gently ; violet-colored vapor escapes, and with it a gas with an odor like that of rotten eggs. At

the same time a yellow coating appears on the inside of the tube above the acid. Add five or six drops more of the acid and continue to heat gently. The bad odor first noticed disappears gradually, and another, quite different odor, irritating to the throat is now perceptible. This is sulphur dioxide, $SO_2$.

## IODIC ACID.

**Experiment 91.**—Pass chlorine into a test-tube containing iodine in suspension in water; or add chlorine water. What becomes of the iodine?

**Experiment 92.**—Add chlorine water to a dilute solution of potassium iodide, and note the successive changes.

**Experiment 93.**—Dissolve iodine in caustic soda. Add an acid to the solution. Explain the changes.

## HYDROFLUORIC ACID.

**Experiment 94.**—In a lead or platinum vessel put a few grams (5–6) of powdered fluor-spar and pour on it enough concentrated sulphuric acid to make a thick paste. Cover the surface of a piece of glass with a thin layer of wax or paraffin, and through this scratch some letters or figures, so as to leave the glass exposed where the scratches are made. Put the glass over the vessel containing the fluor-spar, and let it stand for some hours. Take off the glass, scrape off the coating, and the figures which were marked through the wax or paraffin will be found *etched* on the glass.

## EXPERIMENTS TO ACCOMPANY CHAPTER XIII.

## PROPERTIES OF SULPHUR.

**Experiment 95.**—Distil about 10 grams roll sulphur from an ordinary glass retort. What changes in color and in condition take place? Collect the liquid sulphur formed by the condensation of the vapor in a beaker-glass containing cold water.

**Experiment 96.**—Treat some powdered roll sulphur with carbon disulphide and filter. Does it all dissolve? Try the same experiment with flowers of sulphur. Does this all dissolve? Put the solutions together and allow to evaporate. Examine the crystals deposited. Compare them with some natural crystals of sulphur. See whether one of the crystals will completely dissolve in carbon disulphide.

**Experiment 97.**—In a covered sand or Hessian crucible melt about 25 grams of roll sulphur. Let it cool slowly, and when a thin crust has formed on the surface make a hole through this and pour out the liquid part of the sulphur. What is left? Compare with the crystals formed in the last experiment.—Lay the crucible aside, and in the course of a few days again examine the crystals. What changes, if any, have taken place?

**Experiment 98.**—Add hydrochloric acid to a solution of sodium thiosulphate. What takes place?

**Experiment 99.**—In a wide test-tube heat some sulphur to boiling. Introduce into it small pieces of copper-foil or sheet copper. Or hold a narrow piece of sheet copper so that the end just dips into the boiling sulphur.

**Experiment 100.**—Dissolve some sulphur in concentrated caustic soda. In what form is the sulphur in the solution?

### HYDROGEN SULPHIDE.

**Experiment 101.**—Arrange an apparatus as shown in Fig. 49. Put a small handful of the sulphide of iron, FeS, in the
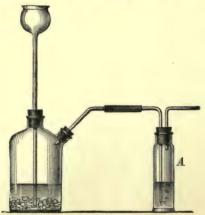


FIG. 49.

flask, and pour dilute sulphuric acid upon it. Pass the evolved gas through a little water contained in the wash cylinder *A*. Pass some of the gas into water. [What evidence have you that it dissolves?] Collect some by displacement of air. Its specific gravity is 1.178. Set fire to some of the gas contained in a cylinder. In this case the air has not free

access to the gas, and the combustion is not complete. The hydrogen burns to form water, while a part of the sulphur is deposited upon the inside walls of the cylinder. If there is free access of air, the sulphur burns to sulphur dioxide and the hydrogen to water.

Make a solution of the gas in water in the usual way. Put some of this in a bottle and set it aside, and in the course of a few days examine it again. Boil another portion for a time in a test-tube, and note the changes. Pass a little of the gas through concentrated sulphuric acid contained in a test-tube, and note the changes. Moisten strips of paper with dilute solutions of lead nitrate, copper sulphate, stannous chloride, antimony chloride, and mercuric chloride; and expose these papers in turn to the gas. What changes take place? Repeat Experiment 90, and see whether one of the gases given off produces similar changes.

**Experiment 102.**—Pass hydrogen sulphide successively through solutions containing a little *lead nitrate, cadmium nitrate,* and *arsenic* prepared by dissolving a little white arsenic, or arsenic trioxide, $As_2O_3$, in dilute hydrochloric acid. What action takes place in each case? The formula of lead nitrate is $Pb(NO_3)_2$; that of cadmium nitrate, $Cd(NO_3)_2$; and that of the chloride of arsenic in solution is $AsCl_3$. The corresponding sulphides are represented by the formulas PbS, CdS, and $As_2S_3$.

## EXPERIMENTS TO ACCOMPANY CHAPTER XIV.

### Manufacture of Sulphuric Acid.

**Experiment 103.**—The manufacture of sulphuric acid can be illustrated in the laboratory by means of the apparatus represented in Fig. 50. This consists of a large balloon flask fitted with a stopper having five openings. By means of tubes it is connected with three small flasks. One of these, *a*, contains water for the purpose of providing a current of steam; another, *c*, contains copper-foil and concentrated sulphuric acid, which give sulphur dioxide when heated; and the third, *b*, contains copper-foil and dilute nitric acid, which give oxides of nitrogen, mainly nitric oxide, NO. When the nitric oxide comes in contact with the air it combines with oxygen, forming nitrogen trioxide and nitrogen peroxide; and when steam and sulphur dioxide are admitted to the flask the reactions

involved in the manufacture of sulphuric acid take place. By means of a pair of bellows attached at $d$ air is supplied. If air is not forced in, the gases become colorless, owing to
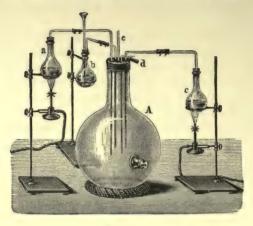


FIG. 50.

complete reduction of the oxides of nitrogen to the form of nitric oxide, NO, which is colorless. If steam is not admitted the walls of the vessel become covered with crystals of nitrosyl-sulphuric acid. This is, however, decomposed by an excess of steam.

**Experiment 104.**—Into a vessel containing ordinary concentrated sulphuric acid introduce small sticks of wood, pieces of paper, and various other organic substances, and note the result. The charring effect is particularly well shown by adding the acid drop by drop to a concentrated solution of sugar, or to molasses, and stirring.

**Experiment 105.**—Sulphuric acid is detected in analysis by adding barium cloride to its solution, when insoluble barium sulphate is formed.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$$

Other insoluble sulphates are those of strontium and lead ; and calcium sulphate is difficultly soluble. To a dilute solution of sulphuric acid or of any soluble sulphate, add in testtubes barium chloride, strontium nitrate, and lead nitrate.

## SULPHUROUS ACID AND SULPHUR DIOXIDE.
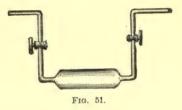
**Experiment 106.**—Put eight or ten pieces of sheet copper, one to two inches long and about half an inch wide, in a 500 cc. flask ; pour 15 to 20 cc. concentrated sulphuric acid on it. On heating, sulphur dioxide will be evolved. The moment the gas begins to come off, lower the flame, and keep it at such a height that the evolution is regular and not too active. Pass some of the gas into a bottle containing water. The solution in water is called sulphurous acid.

**Experiment 107.**—Pass sulphur dioxide into a moderately dilute solution of potassium hydroxide, until the solution is saturated. What is then contained in the solution? To a little of it add hydrochloric acid. What takes place?

**Experiment 108.**—Try the effect of heating concentrated sulphuric acid with charcoal, and with sulphur.

**Experiment 109.**—Collect by displacement of air some of the gas made in Experiment 106. Does it burn? or does it support combustion?

**Experiment 110.**—Pass some of the gas through a bent-glass tube surrounded by a freezing mixture of salt and ice. Tubes provided with glass stop-cocks are made for such pur-



FIG. 51.

poses. They generally have the form represented in Fig. 51. If the tube is taken out of the freezing mixture, the liquid sulphur dioxide changes rapidly to gas, if the tube is open.

**Experiment 111.**—Burn a little sulphur in a porcelain crucible under a bell-jar. Place over the crucible on a tripod some flowers. In the atmosphere of sulphur dioxide the flowers will be bleached.

## SULPHUROUS ACID IS A REDUCING AGENT.

**Experiment 112.**—To a dilute solution of potassium iodide in a test-tube gradually add chlorine water until the solution

becomes clear and colorless. Now add a solution of sulphurous acid. At first iodine is deposited, but on further addition of sulphurous acid it dissolves again. Explain all the changes.

### Sulphur Trioxide.

**Experiment 113.**—Heat a little fuming sulphuric acid gently in a test-tube. What takes place? Put a little of the acid (5–10 cc.) in a small dry retort provided with a glass stopper and connect with a dry glass receiver. Heat the retort gently, and keep the receiver cool. By means of a dry glass rod take out some of the substance which collects in the receiver and put it in water. Lay a little of it on a piece of wood and on a piece of paper.

**Experiment 114.**—Prepare finely divided platinum by moistening some fine asbestos with a solution of platinic chloride and heating to redness in a porcelain crucible. The substance thus obtained is known as platinized asbestos. Now arrange an apparatus so that both oxygen and sulphur dioxide can be passed together through a tube of hard glass as represented in Fig. 52. First pass the two dried gases



Fig. 52.

together through the empty tube and heat a part of the tube by means of a burner. Is there any evidence of combination? Now stop the currents of the gases, let the tube cool down, and introduce a small layer of the platinized asbestos. Pass the dried gases over the heated asbestos. What takes place?

### EXPERIMENTS TO ACCOMPANY CHAPTER XV.

### Preparation of Nitrogen.

**Experiment 115.**—Place a good-sized stoppered bell-jar over water in a pneumatic trough. In the middle of a flat cork about three inches in diameter fasten a small porcelain crucible, and place this on the water in the trough. Put in

it a piece of phosphorus about twice the size of a pea, and set fire to it. Quickly place the bell-jar over it. At first some air will be driven out of the jar. The burning will continue for a short time, and then gradually grow less and less active, finally stopping. On cooling, it will be found that the volume of gas is less than four fifths the original volume, for the reason that some of the air was driven out of the vessel at the beginning of the experiment. Before removing the stopper of the bell-jar see that the level of the liquid outside is the same as that inside. Try the effect of introducing successively several burning bodies into the nitrogen,—as, for example, a candle, a piece of sulphur, phosphorus, etc.
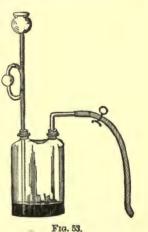
**Experiment 116.**—Place a live mouse in a trap in a bell-jar over water. When the oxygen is used up the mouse will die. After the animal gives plain signs of discomfort, it may be revived by taking away the bell-jar and giving it a free supply of fresh air.

**Experiment 117.**—Pass air slowly over copper contained in a tube heated to redness and collect the gas which passes through. Does it act like nitrogen?

**Experiment 118.**—In a good-sized Wolff's bottle provided with a safety-funnel and delivery-tube as shown in Fig. 53 put some copper-turnings and pour upon them concentrated ammonia, but not enough to cover them. Close the delivery-tube by means of a pinch-cock; and let the vessel stand. What evidence of action is there? After a time, force some of the gas out of the bottle by pouring water through the funnel, and opening the delivery-tube. Does the gas act like nitrogen?

FIG. 53.

## ANALYSIS OF AIR.

**Experiment 119.**—Arrange an apparatus as in Fig. 25. Instead of a plain tube, use one graduated into cubic centimeters. Enclose 60 to 80 cc. air in the tube over water. Arrange the tube so that the level of the water inside and outside is the same. Note the temperature of the air and the

height of the barometer. Reduce the observed volume to standard conditions. Now introduce a piece of phosphorus, as in Experiment 26, and allow it to stand for twenty-four hours. Draw out the phosphorus. Again arrange the tube so that the level of the water inside is the same as that outside. Make the necessary corrections for temperature, pressure, and the tension of aqueous vapor. It will be found that the volume has diminished considerably, but that about four fifths of the gas originally put in the tube is still there. If the work is done properly, the volume of the gas left in the tube will be to the total volume used as 79 to 100. In other words, of every 100 cc. air used 21 cc. are absorbed by phosphorus, and 79 cc. are not. The gas absorbed is oxygen, identical with the oxygen made from the oxide of mercury, manganese dioxide, and potassium chlorate. The gas left over has no chemical properties in common with oxygen. Carefully take the tube out of the vessel of water, closing its mouth with the thumb or some suitable object to prevent the contents from escaping. Turn it with the mouth upward, and introduce into it a burning stick. Does it support combustion ? Is it oxygen ?

**Experiment 120.**—Expose a few pieces of calcium chloride on a watch-glass to the air. It gradually becomes liquid by absorbing water from the air.

**Experiment 121.**—Expose some clear lime-water to the air. It soon becomes covered with a white crust. A similar change takes place if baryta-water is exposed in the same way. Lime-water is made by putting a few pieces of quick-lime in a bottle and pouring water upon it. The mixture is well shaken up and allowed to stand. The undissolved substance settles to the bottom, and with care a clear liquid can be poured off the top. This is lime-water, which is a solution of calcium hydroxide, $Ca(OH)_2$, in water. Baryta-water is a solution of a similar compound of the element barium. When these solutions are exposed to nitrogen or oxygen, or to an artificially prepared mixture of the two gases, no change takes place. Further, if air is first passed through a solution of caustic soda it no longer has the power to cause the formation of a crust on lime-water or baryta-water.

**Experiment 122.**—Arrange an apparatus as shown in Fig. 54. The wash-cylinders $A$ and $B$ are half filled with ordinary caustic-soda solution. The bottle $C$ is filled with water.

The tube *D*, which should be filled with water and provided with a pinch-cock, acts as a siphon. Open the pinch-cock and let the water flow slowly out of the bottle. As it flows out air will be drawn in through the caustic soda in the wash-

cylinders. When the bottle is a quarter filled with air pour some water in again until it is full. Then draw all the water off. Now remove the stopper from the bottle, pour in 20 to 30 cc. lime-water and cork the bottle. The crust formed on the lime-water will now be hardly, if at all, perceptible. There is, therefore, something present in the air under ordinary circumstances which has the power to form a crust on lime-water or baryta-water, and which can be removed by passing the air through caustic soda. Thorough examination has shown that this is the compound which chemists call *carbon dioxide,* and which is commonly known as *carbonic acid gas.* It is the substance which was obtained by burning charcoal in oxygen.
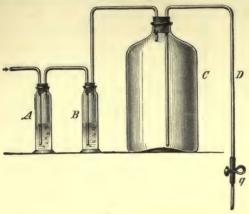
**Experiment 123.**—Into the bottle containing the air from which the carbon dioxide has been removed hold a burning stick or taper for a moment. Notice whether a crust is now formed on the lime-water. Wood and the material from which the taper is made contain carbon. Explain the formation of the crust on the lime-water after the stick of wood or taper has burned for a short time in the vessel.

**Experiment 124.**—Arrange an apparatus as shown in Fig. 55. The bottle *A* contains air. *B* contains concentrated sulphuric acid, *C* contains granulated calcium chloride, *D* is care-

fully dried and contains a few pieces of granulated calcium chloride and air. Pour water through the funnel-tube into *A*, when the air will be forced through *B* and *C* and into *D*. But in passing through *B* and *C* the moisture contained in it
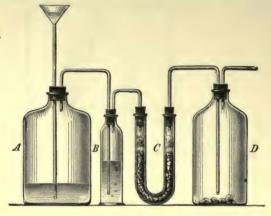


FIG. 55.

will be removed, and the air which enters *D* will be dry. After *A* has once been filled with water, empty it and fill it again, letting the dried air pass into *D*. This operation may be repeated indefinitely. The calcium chloride in *D* will not grow moist.

## EXPERIMENTS TO ACCOMPANY CHAPTER XVI.
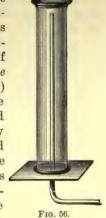
### PREPARATION AND PROPERTIES OF AMMONIA.

**Experiment 125.**—To a little ammonium chloride on a watch-glass add a few drops of a strong solution of caustic soda, and notice the odor of the gas given off. Do the same thing with caustic potash. Mix small quantities of ammonium chloride and lime in a mortar, and add a few drops of water.

**Experiment 126.**—Mix 20 parts iron filings, 1 part potassium nitrate, and 1 part solid potassium hydroxide, and heat the mixture in a test-tube. Is there any evidence of the formation of ammonia?

**Experiment 127.**—Arrange an apparatus as shown in Fig. 45. In the flask put a mixture of 100 grams slaked lime and 50 grams ammonium chloride. Heat on a sand-bath.

After the air is driven out, the gas will be completely ab-
sorbed by the water in the first Wolff's
flask if shaken from time to time. Dis-
connect the delivery-tube from the series
of Wolff's flasks, and connect with an-
other tube bent upward. Collect some of
the gas by displacement of air, *placing the
vessel with the mouth downward.* (Why?)
The arrangement is shown in Fig. 56. The
vessel in which the gas is collected should
be dry, as water absorbs ammonia very
readily. Hence, also, it cannot be collected
over water. In the gas collected introduce
a burning stick or taper. Ammonia does
not burn in air, nor does it support com-
bustion. In working with the gas great care
must be taken to avoid inhaling it in any

Fig. 56.

quantity. After enough has been collected in cylinders to
exhibit the chief properties, connect the delivery-tube again
with the series of Wolff's flasks, and pass the gas through the
water as long as it is evolved.

## Ammonia Burns in Oxygen.

**Experiment 128.**—Put a little of a concentrated solution
of ammonia in a flask placed upon a tripod. Heat gently and,
from a gasometer, pass a rapid current of oxygen through a
bent tube into the liquid. Apply a light to the mouth of the
vessel, when the ammonia will be seen to burn.

## Ammonia forms Ammonium Salts with Acids.

**Experiment 129.**—Put 100 cc. *dilute* ammonia solution in
an evaporating-dish. Try its effect on red litmus paper.
Slowly add dilute hydrochloric acid until the alkaline reaction
is destroyed and the solution is neutral. Evaporate to dry-
ness on a water-bath. Compare the substance thus obtained
with sal-ammoniac, or ammonium chloride. Taste. Heat
on a piece of platinum foil. Treat with a caustic alkali.
Treat with a little concentrated sulphuric acid in dry test-
tubes. Do they appear to be identical? Similarly sulphuric
acid and ammonia yield ammonium sulphate; nitric acid and
ammonia yield ammonium nitrate; etc.

**Experiment 130.**—Fill a dry cylinder with ammonia gas, and another of the same size with hydrochloric acid gas. Bring them together with their mouths covered. Quickly remove the covers, when a dense white cloud will appear in and about the cylinders. This will soon settle on the walls of the vessels as a light white solid. It is ammonium chloride. Thus, from two colorless gases we get a solid substance by an act of chemical combination. Heat is evolved in the act of combination.

## COMPOSITION OF AMMONIA.

**Experiment 131.**—This experiment should be performed by a person experienced in the use of chemical apparatus. A glass-tube, such as represented in Fig. 57, provided with a glass stop-cock is needed. Fill this tube with chlorine free from air over a saturated solution of sodium chloride. After
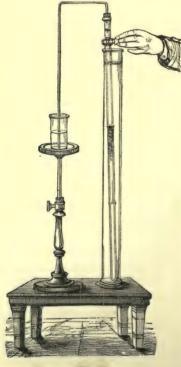


Fig. 57.

it is filled let it stand for some time mouth downward in the solution of sodium chloride to let the liquid drip out of it. Close the stop-cock and remove it from the solution. Hold the tube mouth upward, and pour a concentrated solution of ammonia into the funnel-like projection above the stop-cock, put in the glass stopper, and now by slightly opening the stop-cock let the ammonia pass drop by drop into the tube. Reaction between the chlorine and the ammonia takes place, accompanied by a marked evolution of heat, and in a partly-darkened room light is seen. Great care must be taken not to admit air with the ammonia. After nearly all the ammonia has passed in from the funnel, pour into the funnel about two thirds as much ammonia as has already been used, and let this

in gradually. Leave the stop-cock closed, and fill the funnel with dilute sulphuric acid. Fit a bent tube into a cork, fill this tube with dilute sulphuric acid; put the cork in the funnel, and the other end of the tube in a small beaker containing dilute sulphuric acid, and, after immersing the long tube in water of the ordinary temperature, open the stop-cock. If the operation has been carried out as it should be, the dilute acid will flow into the tube until it is two thirds full, and will then stop. The residual gas is nitrogen. What evidence in regard to the composition of ammonia is furnished by this experiment?

The arrangement of the apparatus in the last stage of the experiment is shown in Fig. 57.

## PREPARATION AND PROPERTIES OF NITRIC ACID.

**Experiment 132.**—Arrange an apparatus as shown in Fig. 58. In the retort put 20 grams sodium nitrate (Chili salt-
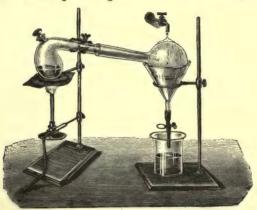


FIG. 58.

peter) and 20 grams concentrated sulphuric acid. On gently heating, nitric acid will distil over, and be condensed in the receiver. After the acid is all distilled off, remove the contents of the retort. Recrystallize the substance from water, and compare it with the sodium sulphate obtained in the preparation of hydrochloric acid. (See Experiment 74.) In the latter stage of the operation the vessels become filled with a reddish-brown gas. The acid which is collected has a somewhat yellowish color.

**Experiment 133.**—Mix together 400 grams concentrated sulphuric acid and 80 grams ordinary concentrated nitric acid. Pour the sulphuric acid into the nitric acid. Distil the mixture from a retort arranged as in the preceding experiment, taking care to keep the neck of the retort cool by placing filter-paper moistened with cold water on it. Use the acid thus obtained for the purpose of studying the properties of pure nitric acid.

### Nitric Acid gives up Oxygen readily, and is hence a good Oxidizing Agent.

**Experiment 134.**—Pour concentrated nitric acid into a wide test-tube, so that it is about one-fourth filled. Heat the end of a stick of charcoal of proper size, and, holding the other end with a forceps, introduce the heated end into the acid. It will continue to burn with a bright light, even though it is placed below the surface of the liquid. The action is oxidation. The charcoal in this case finds the oxy-



FIG. 59.

gen in the acid and not in the air. Great care must be taken in performing this experiment. The charcoal should not come in contact with the sides of the test-tube. A large beaker-glass should be placed beneath the test-tube, so that in case it breaks the acid will be caught and prevented from doing harm. The arrangement of the apparatus is shown in Fig. 59.

The gases given off from the tube are offensive and poisonous. Hence this experiment as well as all others with nitric acid should be carried on under a hood in which the draught is good.

**Experiment 135.**—Boil a little strong nitric acid in a testtube in the upper part of which some horse-hair has been introduced in the form of a stopper. The horse-hair will take fire and burn, and leave a white residue. Hold the test-tube with a forceps over a vessel to catch the contents should the tube break.

**Experiment 136.**—In a small flask put a few pieces of granulated tin. Pour on this just enough strong nitric acid to cover it. Heat gently over a small flame. Soon action will take place. Colored gases will be evolved, the tin will disappear, and in its place will be found a white powder. This consists mostly of tin and oxygen. (See Experiment 13.)

## METALS DISSOLVE IN NITRIC ACID, FORMING NITRATES.

**Experiment 137.**—Dissolve a few pieces of copper-foil in ordinary commercial nitric acid diluted with about half its volume of water. The operation should be carried on in a good-sized flask and under an efficient hood. When the copper has disappeared, pour the blue solution into an evaporating-dish, and evaporate down to crystallization. Compare the substance thus obtained with copper nitrate. Heat specimens of each. Treat small specimens with sulphuric acid. What evidence have you that the two substances are identical?

## NITRATES ARE DECOMPOSED BY HEAT.

**Experiment 138.**—Heat some potassium nitrate in a testtube. Introduce a piece of wood with a spark on it. Heat also lead nitrate, copper nitrate, and any other nitrates which may be available. What difference do you observe between the decomposition of potassium nitrate and that of lead nitrate?

## NITRATES ARE SOLUBLE IN WATER.

**Experiment 139.**—Try the solubility in water of the nitrates used in the last experiment.

### NITRIC ACID IS REDUCED TO AMMONIA BY NASCENT HYDROGEN.

**Experiment 140.**—In a good-sized test-tube treat a few pieces of granulated zinc with dilute sulphuric acid. What is evolved? Prove it. Now add drop by drop dilute nitric acid. The hydrogen ceases to be given off. Pour the contents of the tube into an evaporating-dish and evaporate the liquid. Put the residue into a test-tube and add caustic-soda solution, when the smell of ammonia will be noticed. Try the action of the gas on red litmus-paper. Moisten the end of a glass rod with a little hydrochloric acid, and hold it in the tube. White fumes are seen. What are they? Do the same with nitric acid. What are the fumes in this case?

### NITROUS ACID.

**Experiment 141.**—Melt 25 grams potassium nitrate in a shallow iron plate and gradually add 50 grams metallic lead cut in small pieces. Stir them together as thoroughly as possible. After the mass is cooled down, break it up and treat with water in a flask. The potassium nitrite will dissolve, while the lead oxide and unused lead will not dissolve. Filter. Add a little sulphuric acid to some of the solution. A colored gas will be given off. See whether a solution of potassium nitrate acts in the same way. Treat with sulphuric acid a little of the residue left after heating potassium nitrate alone in a test-tube as in Experiment 138.

### NITROUS OXIDE.

**Experiment 142.**—In a retort heat 10 to 15 grams crystallized ammonium nitrate until it has the appearance of boiling. Do not heat higher than is necessary to secure a regular evolution of gas. Connect a wide rubber tube directly with the neck of the retort and collect the evolved gas over water, as in the case of oxygen. It supports combustion almost as well as pure oxygen. Try experiments with wood, a candle, and a piece of phosphorus.

## NITRIC OXIDE.

**Experiment 143.**—Arrange an apparatus as shown in Fig. 60.  In the flask put a few pieces of copper-foil.  Cover this with water.  Now add slowly, waiting each time for the action to begin, *ordinary* concentrated nitric acid.  When enough nitric acid has been added gas will be evolved.  If the acid is added rapidly, it not unfrequently happens that the evolution of gas takes place too rapidly, so that the liquid is forced out of the flask through the funnel-tube.  This can be avoided by not being in a hurry.  At first the vessel becomes filled with a reddish-brown gas, but soon the gas evolved becomes colorless.  Collect over water two or three vessels full.  The gas collected is principally nitric oxide, NO, though it is frequently mixed with a considerable quantity of nitrous oxide.
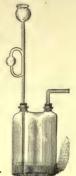


FIG. 60.

**Experiment 144.**—Turn one of the vessels containing colorless nitric oxide with the mouth upward, and uncover it. The colored gas is at once seen, presenting a very striking appearance.  Do not inhale the gas.  Perform the experiments with nitric oxide where there is a good draught.

**Experiment 145.**—Pass nitric oxide into a concentrated solution of ferrous sulphate.  Afterwards heat the solution and collect the gas.  What do you conclude that the gas is?

## NITROGEN TRIOXIDE.

**Experiment 146.**—In a flask fitted with a safety-funnel and a delivery-tube pour nitric acid of specific gravity 1.30–1.35 upon coarsely granulated arsenious oxide, $As_2O_3$.  Heat gently, and conduct the gases through a tube surrounded by a freezing mixture, as in Experiment 110.
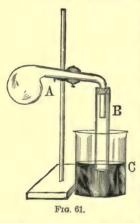
## NITROGEN PEROXIDE.

**Experiment 147.**—Admit a little air to nitric oxide contained in a bell-jar over water, and let the vessel stand. Almost immediately the color will disappear, showing that the nitrogen peroxide formed is decomposed.  Again admit air,

and let the vessel stand. The same changes will be noticed as in the first instance. If oxygen is used instead of air the above changes can be repeated over and over again. Devise an experiment for the purpose of determining whether the nitric oxide is gradually used up or not.

## EXPERIMENTS TO ACCOMPANY CHAPTER XVII.
### PHOSPHORUS.

**Experiment 148.**—[This, as well as the other experiments with phosphorus, should be performed only by an experienced person.] Arrange an apparatus as shown in Fig. 61. The neck of the retort is somewhat drawn out and bent downward and fitted air-tight by means of a cork to the wide glass tube *B.* Some small pieces of ordinary phosphorus are now care-



Fig. 61.

fully slipped into the retort—as much as is obtained by cutting up two sticks three to four inches long. The apparatus is then adjusted as shown in the figure, so that the end of the tube *B* dips below the surface of the water in the beaker *C.* The whole is then allowed to stand for some hours. The oxygen is absorbed from the air contained in the vessel, and the water rises in *B.* Without uncovering the end of *B,* replace the water in *C* by some that has a temperature of about 50°. Now heat the retort gradually, when the phosphorus will distil over and condense in *C* in the molten condition. By lowering the heat gradually at the end of the operation it can finally be stopped without danger of breaking.

**Experiment 149.**—Dissolve a little ordinary phosphorus in carbon disulphide. Pour some of this solution upon a strip of filter-paper, and let this hang in the air or wave it gently in the air. After the carbon disulphide has evaporated the phosphorus will take fire.

**Experiment 150.**—Bring together in a porcelain crucible or evaporating-dish a little phosphorus and iodine. It will be seen that simple contact is sufficient to cause the two sub-

stances to act upon each other. Direct combination takes place, and the action is accompanied by light and heat.
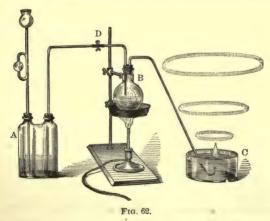
### PHOSPHORUS ABSTRACTS OXYGEN FROM OTHER SUBSTANCES.

**Experiment 151.**—Add a little of a solution of phosphorus in carbon disulphide to a solution of copper sulphate. What change takes place?

**Experiment 152.**—Put a few pieces of ordinary phosphorus in a glass tube and seal it. Heat gradually to 300°. Open the tube and examine the product. See whether it takes fire as readily as ordinary phosphorus does; whether it dissolves in carbon disulphide; whether it melts easily when put in water heated to between 45° and 50°.

### PHOSPHINE.

**Experiment 153.**—Arrange an apparatus as shown in Fig. 62. In the small flask *B* put about 5 grams caustic potash dis-



Fig. 62.

solved in 10–15 cc. water, and *when the solution is cold* add a few small pieces of phosphorus the size of a pea. Pass hydrogen for some time through the apparatus from the generating-flask *A* until all the air is displaced; then disconnect at *D*, leaving the rubber tube, closed by the pinch-cock, on the tube which enters the flask. Gently heat the contents of the retort, when gradually a gas will be evolved, and will escape through the water in *C*. As each bubble comes in contact
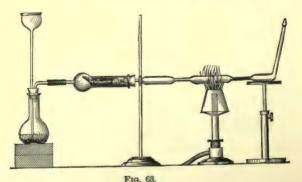
with the air it takes fire, and the products of combustion ar
range themselves in rings, which become larger as they rise.
They are extremely beautiful, particularly if the air of the
room is quiet. Both the phosphorus and the hydrogen com-
bine with oxygen in the act of burning. Collect some of the
gas in a tube over water, and then place the tube mouth up-
ward. What difference is there between the burning of the
gas under these circumstances, and that noticed when the
rings are formed? Collect another tube full of the gas, and
let this stand for some time. Then open the vessel by taking
it out of the water. Has any change taken place in the gas?

### Arsenic.

**Experiment 154.**—Heat a small piece of arsenic on charcoal
in the flame of the blow-pipe.

### Arsine.

**Experiment 155.**—Arrange an apparatus as shown in Fig.
63. Put some pure granulated zinc in the flask and pour



Fig. 63.

dilute sulphuric acid on it. The calcium-chloride tube serves
to dry the gas. When the air is all out of the vessel and the
hydrogen is lighted, add slowly a little of a solution of arsenic
trioxide, $As_2O_3$, in dilute hydrochloric acid. The appearance
of the flame will soon change. It will become paler, with a
slightly bluish tint, and give off white fumes. (See next ex-
periment.)

## Marsh's Test for Arsenic.

**Experiment 156.**—Into the flame of the burning hydrogen and arsine produced in the last experiment introduce a piece of porcelain, as the bottom of a small porcelain dish or a crucible, and notice the appearance of the spots. Heat by means of a Bunsen burner the tube through which the gas is passing, which should be of hard glass. Just beyond the heated place there will be deposited a thin layer of metallic arsenic, commonly called a *mirror of arsenic*. This deposit is due to the direct decomposition of the arsine into arsenic and hydrogen by heat. [Compare ammonia, phosphine, and arsine with reference to their stability.]

### Antimony.

**Experiment 157.**—Heat a small piece of antimony on charcoal in the blow-pipe flame. Try the action of dilute and of concentrated hydrochloric acid, of dilute and of concentrated nitric acid, and of a mixture of the two acids on a small piece of antimony.

### Stibine.

**Experiment 158.**—Stibine is made by the same method as that used in making arsine. Make some, using a solution of tartar emetic. Introduce a piece of porcelain in the flame, and afterwards heat the tube through which the gas is passing. Compare the antimony spots with the arsenic spots. Color? Volatility? Conduct towards a solution of sodium hypochlorite or hypobromite?

### Bismuth.
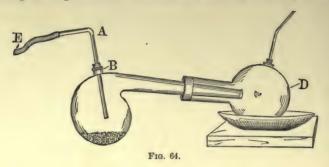
**Experiment 159.**—Heat a piece of bismuth on charcoal in the blow-pipe flame. See how it conducts itself towards hydrochloric acid; towards nitric acid. If a solution is obtained in either case, add water to it. Explain what takes place.

### Phosphorus Trichloride.

The experiments with the chlorides of phosphorus must be carried on under a hood or out-of-doors.

**Experiment 160.**—Arrange an apparatus as shown in Fig. 64. The tube *A* is arranged so that it can be raised or lowered in the retort. Put 50 to 100 grams ordinary phosphorus in the retort, taking precautions to prevent it from taking fire

during the operation. This is best accomplished by fitting



FIG. 64.

corks in both openings of the retort; placing the retort in a vessel of cold water; removing the cork from *B*, throwing in a piece of phosphorus, and quickly putting the cork in. The pieces must not be put in in too rapid succession. After all the phosphorus is in the retort, adjust the apparatus as represented, placing the receiver *D* in a dish of cold water. Now connect by means of the rubber tube *E* with an apparatus furnishing chlorine, dried by means of concentrated sulphuric acid and calcium chloride. As soon as the chlorine comes in contact with the phosphorus action begins, and the product, which is phosphorus trichloride, distils over into the receiver. If the action is taking place too rapidly, the inside of the retort will become covered with a coating of red phosphorus. In this case raise the tube *A* a little and the red coating will gradually disappear. If the tube is raised too high, not enough heat is generated, and the trichloride in the retort is converted into the pentachloride, which is deposited as a white coating.



FIG. 65.

By raising and lowering the tube according to the indications, the retort can be kept clear, and all the phosphorus converted into the trichloride. This manipulation of the tube is much facilitated by fitting into the cork a somewhat larger tube, through which the smaller one can pass easily; letting this project about an inch and an half above the cork and passing over it a piece of rubber tubing of such size that while the smaller tube moves through it readily, the two form a gas-tight joint. This is shown in Fig. 65. After the

operation is finished, pour the liquid from the receiver into a clean dry flask, and distil on a water-bath. Try the action of a little of the compound on water.

## PHOSPHORUS PENTACHLORIDE.

**Experiment 161.**—Put the trichloride of phosphorus obtained in the last experiment in a wide-mouthed bottle surrounded by cold water. Through a wide glass tube pass dry chlorine upon the surface of the liquid, and as the action advances, and a solid begins to make its appearance, stir the contents of the bottle. Continue the passage of the chlorine until the product is a perfectly dry solid. The arrangement of the bottle containing the trichloride, and that of the delivery-tube, is shown in Fig. 66. The bottle is put in a larger vessel containing cold water, which is renewed from time to time during the process.
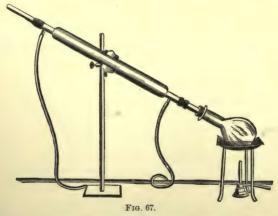


FIG. 66.

Try the action of a little phosphorus pentachloride on water. In a large dry flask heat a little of the pentachloride.

## EXPERIMENTS TO ACCOMPANY CHAPTER XVIII.

### PHOSPHORIC ACID.

**Experiment 162.**—In a flask connected with an inverted



FIG. 67.

condenser, as shown in Fig. 67, boil 10 to 15 grams of ordinary phosphorus with 250 cc. ordinary commercial nitric acid. If

necessary, add more acid after a time. Boil gently until the phosphorus disappears. Evaporate the solution to complete dryness, so as to get rid of all the nitric acid. Dissolve a little of the product in water, and add a few drops of the solution to a dilute solution of silver nitrate. What effect is produced? Heat some of the product gently in a porcelain crucible, and from time to time take out a little, dissolve it in water, and try its action on silver nitrate.

**Experiment 163.**—Try the action of ordinary sodium phosphate on silver nitrate. Heat a little of the salt in a porcelain crucible to redness. After cooling, try the action of the salt left in the crucible on silver nitrate.

### Arsenic Acid.

**Experiment 164.**—Pass chlorine into water containing arsenic trioxide in suspension, until the oxide is dissolved. Evaporate to crystallization. Into a dilute solution of the product thus obtained, to which some hydrochloric acid is added, pass hydrogen sulphide. Explain the changes.

### Reduction of Arsenic Trioxide.

**Experiment 165.**—In the bottom of a dry tube of hard glass of the form represented in Fig. 68 put a minute piece of arsenic trioxide, and just above it a small bit of charcoal. Heat gently. Explain the change.

### Sulphides of Arsenic.

**Experiment 166.**—Pass hydrogen sulphide into a dilute solution of arsenic trioxide in hydrochloric acid.— Filter off the precipitate, and try the action of ammonium sulphide on some of it.

### Sulphides of Antimony.

**Experiment 167.**—Pass hydrogen sulphide into a solution of antimonic acid made by treating antimony with *aqua regia* and diluting with water. Pass hydrogen sulphide into a solution of antimony trichloride made by dissolving stibnite or antimony trisulphide in hydrochloric acid. Try the action of ammonium sulphide on the precipitates after filtering.



Fig. 68.

### Oxychlorides of Antimony.

**Experiment 168.**—Treat a solution of antimony trichloride with water.

## Basic Nitrates of Bismuth.

**Experiment 169.**—Dissolve a little bismuth in nitric acid and evaporate. Add water.

## Boron.

**Experiment 170.**—Make a hot solution of 30 grams crystallized borax in 120 cc. water. Add *slowly* 10 grams concentrated sulphuric acid. On cooling, the boric acid will crystallize out. What evidence have you that the substance which crystallizes out of the solution is not borax? Try the solubility in alcohol of specimens of each. Is there any difference? Treat a few crystals of borax with about 10 cc. alcohol; pour off the alcohol and set fire to it. Treat a few crystals of the boric acid in the same way. What difference do you observe? Distil an aqueous solution of boric acid, and determine whether any of the acid passes over with the water vapor.

### EXPERIMENTS TO ACCOMPANY CHAPTER XIX.

#### Carbon.—Bone-black Filters.

**Experiment 171.**—Make a filter of bone-black by fitting a paper filter into a funnel 12 to 15 mm. (5 to 6 inches) in diameter at its mouth. Half fill this with bone-black. Pour a dilute solution of indigo through the filter. If the conditions are right the solution will pass through colorless. Do the same thing with a dilute solution of litmus. If the color is not completely removed by one filtration, heat and filter again. The color can also be removed from solutions by putting some bone-black into them and boiling for a time. Try this with half a liter each of the litmus and indigo solutions used in the first part of the experiment. Use about 4 to 5 grams bone-black in each case. Shake the solution frequently while heating.

#### Charcoal absorbs Gases.

**Experiment 172.**—Collect over mercury in glass tubes some ammonia gas, and some carbon dioxide. Introduce into each a piece of charcoal, which has been heated in a Bunsen-burner flame in order to drive out gases which may be contained in the pores.

#### Carbon combines with Oxygen to form Carbon Dioxide.

**Experiment 173.**—Put a small piece of charcoal in a piece of hard-glass tube. Heat the tube, and pass oxygen through it.

Pass the gases into clear lime-water.   Arrange the apparatus as shown in Fig. 69.

*A* is a large bottle containing oxygen ; *B* is a cylinder containing sulphuric acid ; *C* is a U-tube containing calcium chloride ; *D* is the hard-glass tube containing the charcoal; *E* is the cylinder with clear lime-water.   Explain all that takes place.

CARBON REDUCES SOME OXIDES WHEN HEATED WITH THEM.

**Experiment 174.**—Mix together two or three grams powdered copper oxide, $CuO$, and about one tenth its weight of powdered charcoal; heat in a hard-glass tube, as shown in Fig. 70, or, still better, use an arsenic-tube.



Pass the gas which is given off into lime-water contained in a test-tube.   Is it carbon dioxide?   What evidence have you that oxygen has been extracted from the copper oxide?   Compare the substance left in the tube with metallic copper. Treat both with nitric acid, with sulphuric acid.

**Experiment 175.**—Repeat Experiment 165 with somewhat larger quantities of the substances, and examine the gas given off.

HYDROCARBONS.

**Experiment 176.**—Make marsh-gas by heating in a retort a

mixture of 20 grams sodium acetate, 20 grams potassium hydroxide, and 30 grams slaked lime. Collect some of the gas over water. Is it a combustible gas?

**Experiment 177.**—Make ethylene as follows : In a flask of 2 to 3 liters capacity put a mixture of 25 grams alcohol and 150 grams ordinary concentrated sulphuric acid. Heat to 160° to 170°, and add gradually through a funnel tube about 500 cc. of a mixture of 1 part of alcohol and 2 parts of concentrated sulphuric acid. Pass the gas through three wash-bottles containing, in order, concentrated sulphuric acid, caustic soda, and concentrated sulphuric acid. Collect some of the gas over water. Is it combustible?

### EXPERIMENTS TO ACCOMPANY CHAPTER XX.

#### Carbon Dioxide is formed when a Carbonate is treated with an Acid.

**Experiment 178.**—In test-tubes add successively dilute hydrochloric, sulphuric, nitric, and acetic acids to a little sodium carbonate. In each case pass the gas given off through lime-water, and insert a burning stick in the upper part of each tube.—Perform the same experiments with small pieces of marble.

#### Preparation and Properties of Carbon Dioxide.

**Experiment 179.**—Arrange an apparatus as shown in Fig. 71. In the flask put some pieces of marble or limestone, and pour ordinary hydrochloric acid on it. The gas should be collected by displacement of air, the vessel being placed with the mouth upward. Collect several cylinders or bottles full of the gas. Into one introduce successively a lighted candle, a burning stick, a bit of burning phosphorus. Into another, if convenient, put a live mouse. With another proceed as if pouring water from it. Pour the invisible gas upon the flame of a burning candle. Pour some of the gas from one vessel to another, and show that it has been transferred. Balance a beaker on a good-sized pair of scales, and pour carbon dioxide into it. If the balance is at all sensitive, the pan on which the beaker is placed will sink.



FIG. 71.

### Carbon Dioxide is given off from the Lungs.

**Experiment 180.**—Force the gases from the lungs through some lime-water by means of an apparatus arranged as shown in Fig. 72.

### Formation of Carbonates.

**Experiment 181.**—Pass carbon dioxide into a solution of potassium hydroxide to saturation. Determine whether a carbonate is in solution or not.

**Experiment 182.**—Pass carbon dioxide into 50 to 100 cc. clear lime-water. Filter off the white insoluble substance. Try the action of a little acid on it. What evidence have you that it is a carbonate?

Fig. 72.

**Experiment 183.**—Pass carbon dioxide first through a little water to wash it, and then into 50 to 100 cc. clear lime-water. Continue to pass the gas for some time after the precipitate is formed. The precipitate dissolves. Heat the solution. What happens? Explain these reactions.

### Preparation and Properties of Carbon Monoxide.

**Experiment 184.**—Put 10 grams crystallized oxalic acid and 50 to 60 grams concentrated sulphuric acid in an appropriate flask. Connect with two Wolff's flasks containing a solution of caustic soda, so that the gas evolved will bubble through the solution. Heat gently. Collect some of the gas over water. Set fire to some, and notice the characteristic blue flame. If convenient put a live mouse in a vessel containing a mixture of about equal parts of carbon monoxide and air. It will die unless taken out.

### Carbon Monoxide is a good Reducing Agent.

**Experiment 185.**—Pass carbon monoxide over some heated copper oxide contained in a hard-glass tube. Is the oxide reduced? How do you know? Is carbon dioxide formed? What evidence have you? Was the carbon monoxide used free of carbon dioxide? If not, what evidence have you that carbon dioxide is formed in this experiment?

**Experiment 186.**—Pass carbon dioxide over heated charcoal in a hard-glass tube. What is formed?
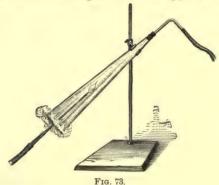
## EXPERIMENTS TO ACCOMPANY CHAPTER XXI.

### COAL-GAS.

**Experiment 187.**—Heat some bituminous coal in a retort and collect over water the gases given off. Are these gases combustible?

### OXYGEN BURNS IN AN ATMOSPHERE OF A COMBUSTIBLE GAS.

**Experiment 188.**—Break off the neck of a good-sized retort; fit a perforated cork to the small end; pass a piece of glass tube through the cork, and connect by means of rubber hose with an outlet for coal-gas. Fix the apparatus in position,



FIG. 73.

as shown in Fig. 73. Turn the gas on, and when the air is driven out of the retort-neck, light the gas. The neck is now filled with illuminating gas, and the gas is burning at the mouth of the vessel. If now a platinum jet from which oxygen is issuing is passed up into the gas the oxygen will take fire, and a flame will appear where the oxygen escapes from the jet. The oxygen burns in the atmosphere of coal-gas.

### KINDLING TEMPERATURE OF GASES.

**Experiment 189.**—Light a Bunsen burner. Bring down upon the flame a piece of brass or iron wire-gauze. There is no flame above the gauze. That the gas passes through unburned can be shown by applying a light just above the outlet of the burner and above the gauze. The gas will take fire and burn. By simply passing through the thin wire-gauze, then, the gas is cooled down below its burning temperature, and does not burn unless it is heated up again. Turn on a Bunsen burner.

Do not light the gas. Hold a piece of wire-gauze about one and a half to two inches above the outlet. Apply a lighted match above the gauze, when the gas will burn above the gauze, but not below it. Here again the heat necessary to raise the temperature of the gas to the burning temperature cannot be communicated through the gauze. If in either of the above-described experiments the gauze is held in position for a time, it will probably become so highly heated that the gas on the side where there is no flame will be raised to the burning temperature. The instant that point is reached the flame becomes continuous.

## The Blow-pipe and its Uses.

FIG. 74.

The blow-pipe used in chemical laboratories is constructed as shown in Fig. 74.

When used with the Bunsen burner it is best to slip into the burner a brass tube ending above in a narrow slit-like opening, as shown in Fig. 75. The tube referred to, marked

FIG. 76.

FIG. 75.

*a* in the figure, reaches to the bottom of the burner, and thus cuts off the supply of air which usually enters the holes at the base. The gas is now lighted, and the current so regulated that there is a small flame about 1½ to 2 inches long. The tip of the blow-pipe is placed on the slit of the burner in the flame, as shown in Fig. 76. By blowing regularly and not violently through the pipe the flame is forced down in the same direction as the end-piece of the blow-pipe, and the slant of the burner-slit. Under proper

conditions the flame separates sharply into a central blue part and an outer part of another color. The direction and lines of division of the flame are indicated in Fig. 76. The outer part of the flame marked *o* is the *oxidizing flame ;* the part marked *r* is the *reducing flame.*

**Experiment 190.**—Select a piece of charcoal about 4 inches long by 1 inch wide and 1 inch thick, with one surface plane.* Near the end of the plane surface make a cavity by pressing the edge of a small thin coin against it, and turning it completely round a few times. Mix together equal small quantities of dry sodium carbonate and lead oxide. Put a little of the mixture in the cavity in the charcoal, and heat it in the reducing flame produced by the blow-pipe. In a short time globules of metallic lead will be seen in the molten mass. After cooling, scrape the solidified substance out of the cavity in the charcoal. Put it in a small mortar, treat it with a little water, and, after breaking it up and allowing as much as possible to dissolve, pick out the metallic beads. Is it malleable or brittle? Is metallic lead malleable or brittle? Is it dissolved by hydrochloric acid? Is lead soluble in hydrochloric acid? Is it soluble in nitric acid? Is lead soluble in nitric acid? The action of the acids can be tried by putting the bead on a small dry watch-glass and adding a few drops of the acid. Does the substance act like lead? What has become of the oxygen with which the lead was combined in the oxide? Is there any special advantage in having a support of charcoal for this experiment?

**Experiment 191.**—Heat a small piece of metallic lead on charcoal in the oxidizing blow-pipe flame. Notice the formation of the oxide, which forms a coating or film on the charcoal in the neighborhood of the metal. Is there any analogy between this process and the burning of hydrogen? In what does the analogy consist? What differences are there between the two processes?

**Experiment 192.**—Repeat the experiments with arsenic, antimony, and bismuth. Notice the colors of the films formed on the charcoal.

**Experiment 193.**—Melt into a bit of glass tubing a piece of platinum wire 8 to 10 mm. (3 to 4 inches long) and bend the end so as to form a small loop, as shown in Fig. 77. Heat the

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* Pieces of charcoal prepared for blow-pipe work can be bought from dealers in chemical apparatus, at small cost.

loop in the flame of a Bunsen burner, and then dip it into some sodium-ammonium phosphate (microcosmic salt). Heat in the oxidizing flame of the blow-pipe until a clear glass bead is formed in the loop. What changes have taken place? and what is the clear glass? Bring a minute particle of a man-



Fig. 77.

ganese compound in contact with the bead, and heat again. What change takes place? Try the same experiment, using successively a cobalt compound, a copper compound, and an iron compound. Now, instead of using microcosmic salt, use borax. Explain the changes in all the above-described experiments.

## CYANOGEN.

**Experiment 194.**—Make potassium cyanide by heating potassium ferrocyanide in an iron crucible.

**Experiment 195.**—Make cyanogen by heating mercuric cyanide. *Cyanogen is poisonous.* Burn some of the gas.

**Experiment 196.**—Make potassium cyanate from some of the cyanide obtained in Experiment 194. This is done by melting it in an iron crucible, and, while the mass is liquid, adding about four times its weight of red lead, stirring during the operation. After this the crucible should again be put in the furnace for a little while, the metallic lead allowed to settle, and the contents poured out on a smooth stone. Break this up, and extract the cyanate with alcohol.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXII.
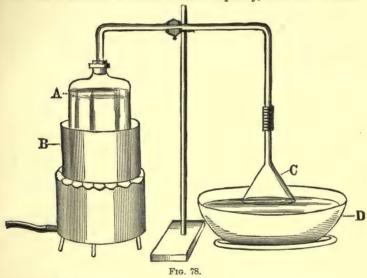
### SILICON.

**Experiment 197.**—Prepare sodium fluosilicate as directed in the next experiment. Mix 3 parts of the dry salt with 1 part of sodium cut in pieces. Throw this mixture all at once into a Hessian crucible heated to bright-red heat in a furnace. Add immediately 9 parts granulated zinc, and a layer of sodium chloride previously heated to drive off water. The crucible is then covered, and the fire allowed to burn down. After cooling, the regulus of zinc containing the silicon is separated from the slag, washed with water, and treated with hydrochloric

acid. The zinc dissolves and leaves the silicon. This is again washed with water and then heated with nitric acid, and washed with water, when crystals of silicon, sometimes of great beauty, are obtained. Try the effect of heating a little of the silicon in the air. Try the action of acids and of alkalies upon it.

### SILICON TETRAFLUORIDE AND FLUOSILICIC ACID.

**Experiment 198.**—Arrange an apparatus as shown in Fig. 78. *A* is a bottle of about 2 liters capacity, such as are com-



FIG. 78.

monly used for transporting acids. This is about two-thirds filled with alternating layers of sand and powdered fluor-spar, moistened with concentrated sulphuric acid. The bottle is put in the deep sand-bath *B*, and connected by means of a wide glass tube with the funnel *C*, which dips just below the surface of the water in the large evaporating-dish *D*. The sand-bath is now gently heated, when silicon tetrafluoride passes over. Coming in contact with water, it is decomposed, silicic acid being deposited and fluosilicic acid passing into solution. In order to prevent clogging, the gelatinous silicic acid is from time to time removed from the mouth of the funnel by means of a bent-glass rod. After the action is complete, filter the solution. Take out one quarter, and to the

rest slowly add a solution of sodium carbonate until the whole just begins to show an alkaline reaction; now add the other quarter of the acid, and filter. Explain all the reactions. Heat a little of the dried salt in a covered platinum crucible. What change takes place? What evidence have you that the change has taken place? To a little of the salt in water add a solution of potassium hydroxide. What change takes place? Dry the silicic acid formed in the first part of the experiment by decomposition of the silicon tetrafluoride.

### Silicic Acid.

**Experiment 199.**—Boil some of the silicic acid obtained in the last experiment with sodium hydroxide. Treat some of the solution with hydrochloric acid ; with ammonium chloride.

**Experiment 200.**—Add some fine sand to about four times its weight of a molten mixture of potassium and sodium carbonates, heated in a platinum crucible in the flame of the blast-lamp. Continue the heating until no more sand is dissolved. Pour the molten mass out on a stone, and when cooled break it up and treat it with water.

**Experiment 201.**—Treat a little of the solution containing sodium and potassium silicates, prepared in the last experiment, with a little sulphuric or hydrochloric acid. A gelatinous substance will be precipitated. This is silicic acid. Some of the acid remains in solution. By evaporating the solution to dryness and heating for a time on the water-bath, all the silicic acid is rendered insoluble.

### EXPERIMENTS TO ACCOMPANY CHAPTER XXIV.

#### Chlorides, Bromides, and Iodides.

**Experiment 202.**—Dissolve a small crystal of silver nitrate in pure water. Add to a small quantity of this solution in a test-tube a few drops of dilute hydrochloric acid. The white substance thus precipitated is silver chloride, $AgCl$. To another small portion of the solution add a few drops of a dilute solution of common salt, or sodium chloride, $NaCl$. The white substance produced in this case is also silver chloride. Add ammonia to each tube. If sufficient is added the precipitates will dissolve. On adding enough hydrochloric acid to these solutions to combine with all the ammonia the

silver chloride is again thrown down. On standing exposed to the light both precipitates change color, becoming finally dark violet. The reactions involved in the above experiments are these : In the first place, when hydrochloric acid is added to silver nitrate this reaction takes place :

$$AgNO_3 + HCl = AgCl + HNO_3.$$

When sodium chloride is added this reaction takes place :

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

In the first reaction nitric acid is set free ; in the second, the sodium and silver exchange places. In addition to the insoluble silver chloride, there is formed at the same time the soluble salt, sodium nitrate. On adding ammonia the silver chloride forms with it a compound which is soluble in water ; and on adding an acid, the ammonia combines with it, leaving the silver chloride uncombined and therefore insoluble.

Extensive use is made of insoluble compounds for the purpose of detecting substances in analysis. The only insoluble chlorides are those of silver, lead, and mercury.* If, therefore, on adding hydrochloric acid or a soluble chloride to a solution, a precipitate is formed, the conclusion is justified that one or more of the three metals—silver, lead, or mercury —is present. By taking account of the differences in the properties of these chlorides it is not difficult to decide of which of them a precipitate consists.

## HYDROXIDES.

**Experiment 203.**—To some pieces of freshly-burnt lime add enough cold water to cover it. The action which takes place is represented by the equation

$$CaO + H_2O = Ca(OH)_2.$$

The process is known as slaking.

**Experiment 204.**—To a small quantity of a dilute solution of magnesium sulphate add a dilute solution of caustic soda. The white precipitate is magnesium hydroxide. [Would you

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* There are two chlorides of mercury. Only one of them, mercurous chloride, is insoluble.

expect this precipitate to be soluble in sulphuric acid? in hydrochloric acid? in nitric acid?] The answers follow from these considerations: When acids act upon hydroxides, salts are formed; magnesium sulphate is soluble, as is seen by the fact that we started with a solution of this salt; the only insoluble chlorides are those of silver, lead, and mercury; all nitrates are soluble.

When a solution of an iron salt is treated with sodium hydroxide a precipitate of iron hydroxide is formed:

$$FeCl_3 + 3NaOH = FeO_3H_3 + 3NaCl.$$

**Experiment 205.**—To a dilute solution of that chloride of iron which is known as ferric chloride add caustic soda. The reddish precipitate which is formed is ferric hydroxide. [From the general statements made above, would you expect this precipitate to be soluble in hydrochloric acid? in nitric acid? Try each. Is it soluble in sulphuric acid?]

**Experiment 206.**—Add to a solution of an aluminium salt sodium hydroxide. After a precipitate is formed continue to add the sodium hydroxide. Perform similar experiments with a chromium and with a lead salt. Boil each of the solutions obtained. Treat a solution of copper sulphate with sodium hydroxide in the cold. Heat.

## Sulphates.

**Experiment 207** —Make a dilute solution of barium chloride, of lead nitrate, of strontium nitrate. To a small quantity of each in a test-tube add a little sulphuric acid. [What remains in solution?] Make a somewhat concentrated solution of calcium chloride. To this add sulphuric acid. [What is in solution?] Add more water, and see whether the precipitate will dissolve. The formulas of the salts used in the experiments are barium chloride, $BaCl_2$; lead nitrate, $Pb(NO_3)_2$; strontium nitrate, $Sr(NO_3)_2$. [Write the equations expressing the reactions.] If to the solutions of the salts any soluble sulphate is added instead of sulphuric acid, the same insoluble sulphates will be formed. The sulphates of iron, copper, sodium, and potassium are among the soluble sulphates. Make dilute solutions of small quantities of each of these, and add them successively to the solutions of barium chloride,

lead nitrate, and strontium nitrate. The formula of iron sulphate is $FeSO_4$; of copper sulphate, $CuSO_4$; of sodium sulphate, $Na_2SO_4$; and of potassium sulphate, $K_2SO_4$. Write the equations representing the reactions which take place in the above experiments. It need hardly be explained that the action consists in an exchange of places on the part of the metals. Thus, when the soluble salt iron sulphate, $FeSO_4$, is brought together with the soluble salt barium chloride, $BaCl_2$, the insoluble salt barium sulphate, $BaSO_4$, and the soluble salt iron chloride, $FeCl_2$, are formed :

$$FeSO_4 + BaCl_2 = FeCl_2 + BaSO_4.$$

## REDUCTION OF SULPHATES TO SULPHIDES.

**Experiment 208.**—Mix and moisten a little sodium sulphate and finely-powdered charcoal. Heat the mixture for some time in the reducing flame. After cooling scrape off the salt, dissolve it in a few cubic centimeters of water, and filter through a small filter. If the change to the sulphide has taken place, sodium sulphide, $Na_2S$, is in solution. A solution of a sulphide when added to a solution containing copper gives a black precipitate of copper sulphide. Try this; also try the action on the solution of the salt of copper of some of the sulphate from which the sulphide was made.

## CARBONATES.

**Experiment 209.**—The formation of carbonates by the addition of soluble carbonates to solutions of salts of metals whose carbonates are insoluble, is illustrated by the following experiments: Make solutions of copper sulphate, iron sulphate, lead nitrate, silver nitrate, calcium chloride, barium chloride. Add to each a little of a solution of a soluble carbonate, as sodium carbonate, potassium carbonate, ammonium carbonate. Note the result in each case. Filter off all the precipitates and prove that they are carbonates. This may be done by treating them with dilute acids, which decompose them, causing an evolution of carbon dioxide, which can be detected by passing a little of it into lime-water. In some of the cases mentioned the insoluble salts formed are basic carbonates, as, for example, those of copper and magnesium. The salts of silver, calcium, and barium are the normal carbonates $Ag_2CO_3$, $BaCO_3$, and $CaCO_3$.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXV.

### POTASSIUM SALTS.

**Experiment 210.**—In preparing potassium iodide from iodine and potassium hydroxide, proceed as follows: To 30 grams iodine use 15 grams hydroxide. Dissolve the latter in 100 cc. water. Add half this solution to the iodine in a porcelain evaporating dish. Now slowly add the rest of the liquid until the color disappears. Concentrate the liquid to a syrupy consistence, add 1 gram finely-powdered charcoal, mix, and evaporate to dryness. The residue is then heated to redness in an iron vessel. After cooling extract with water.

**Experiment 211.**—Potassium iodide can also be prepared by the following method: Bring together in a capsule 200 grams water, 10 grams iron filings, and 40 grams iodine; mix, and heat gently. When the solution has become green, decant, filter, and wash. Now heat the liquid nearly to boiling, and gradually add a solution of 35 grams potassium carbonate in 100 grams water. Filter, wash, and evaporate.

**Experiment 212.**—Dissolve 50 grams potassium carbonate in 500 to 600 cc. water. Heat to boiling in an iron or a silver vessel, and gradually add the slaked lime obtained from 25 to 30 grams of good quicklime. During the operation the mass should be stirred with an iron spatula. After the solution is cool, draw it off by means of a siphon into a bottle. This may be used in experiments in which caustic potash is required.

**Experiment 213.**—Mix together 15 grams potassium nitrate and 2.5 grams powdered charcoal. Set fire to the mass.

**Experiment 214.**—Treat a quantity of wood ashes with water. Filter, and examine by means of red litmus-paper. Evaporate to dryness. What evidence have you that the residue contains potassium carbonate?

### SODIUM SALTS.

**Experiment 215.**—Make a supersaturated solution of sodium sulphate by heating an excess of the salt with water at 33°. Filter the solution into small flasks and cork them. On removing the corks and agitating the vessels, the salt will suddenly crystallize out.

**Experiment 216.**—Pass carbon dioxide into a strong solution of ammonia (about 100 cc.) until it is no longer absorbed.

A solution of acid ammonium carbonate is thus obtained. Add this to a concentrated solution of sodium chloride as long as a precipitate is formed. Filter off the precipitate, and dry it by spreading it upon layers of filter-paper. Heat some of the salt when dry, and determine whether the gas given off is carbon dioxide or not. When gas is no longer given off by heat, let the tube cool and examine the residue.

**Experiment 217.**—Make ammonium sulphide thus : Divide a given quantity of a solution of ammonia into two equal parts. Saturate one half by passing hydrogen sulphide through it, and then add the other half.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXVI.

### CALCIUM SALTS.

**Experiment 218.**—Dissolve 10 to 20 grams of limestone or marble in common hydrochloric acid. Filter, and evaporate to dryness. Expose a few pieces of the residue to the air.

### MAGNESIUM AND ITS SALTS.

**Experiment 219.**—Make anhydrous magnesium chloride thus : Dissolve 180 grams *magnesia usta* in ordinary hydrochloric acid ; shake the solution with an excess of magnesia to remove iron and aluminium ; filter ; add 400 grams ammonium chloride ; evaporate to dryness, keeping the mass constantly stirred. The double salt thus formed must be dried until a small specimen put in a test-tube is found not to give off water when heated. The dry salt is then ignited in a crucible placed in a furnace until ammonium chloride is no longer given off, when the molten mass, which is anhydrous magnesium chloride, is poured out on a stone and, after it is broken up, it is put in a dry bottle provided with a good stopper.

**Experiment 220.**—Mix 6 parts anhydrous magnesium chloride, 1 part of a mixture of sodium and potassium chlorides, prepared by melting the two together and breaking up after cooling, 1 part powdered fluor-spar, and 1 part sodium. Throw this mixture all at once into a red-hot crucible in a furnace, and cover the crucible. In a few moments a curious sound is heard, and this indicates that the reaction is taking place. Now take the crucible out of the furnace, and stir the liquid in it with the aid of a clay pipe-stem. This causes the

particles of the metal to collect in one large spherical mass. After cooling, break the crucible, separate the metallic ball from the slag, and wash it quickly with hydrochloric acid to remove superficial impurities. If the slag is melted with a quarter the weight of sodium that was used at first, a second smaller piece of magnesium will be obtained.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXVII.

### ALUMINIUM CHLORIDE.

**Experiment 221.**—Aluminium chloride is made thus: Mix aluminic oxide with starch-paste; form the mass into small balls of the size of ordinary marbles; ignite these in a crucible in a furnace; put them in a porcelain tube, and then pass dry chlorine over them, at the same time heating the tube to redness. The chloride will sublime in the front end of the tube or in a receiver if the heat is sufficient. It can be purified by subliming it over heated iron or aluminium.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXVIII.

### COPPER AND ITS SALTS.

**Experiment 222.**—Cuprous chloride is best made as follows: Saturate a solution of 1 part sodium chloride and $2\frac{1}{2}$ parts crystallized copper sulphate with sulphur dioxide. Filter, and wash with acetic acid.

### SILVER AND ITS SALTS.

**Experiment 223.**—Dissolve a ten or twenty-five cent piece in dilute nitric acid. Dilute the solution to 200 to 300 cc. with hot water. Add a hot solution of common salt until it ceases to produce a precipitate. Filter off the white silver chloride and wash with hot water. Dry the precipitate on the filter, by placing the funnel with the filter and precipitate in an air-bath heated to about 110°. Remove the precipitate from the filter and put it into a porcelain crucible. Heat gently with a small flame until the chloride is melted; then let it cool. Cut out a piece of sheet zinc large enough to cover the bottom of the crucible, and lay it on the silver chloride. Now add a little water and a few drops of dilute

sulphuric acid, and let the whole stand for twenty-four hours. The silver chloride is reduced to silver, and zinc chloride is formed:

$$Zn + 2AgCl = ZnCl_2 + 2Ag.$$

Take out the piece of zinc and wash the silver with a little dilute sulphuric acid, and then with water. Dissolve the silver in dilute nitric acid and evaporate to dryness on the water-bath, so that all the nitric acid is driven off. Dissolve the residue in water, and put the solution either in a bottle of dark glass or one wrapped in dark paper.

**Experiment 224.**—To a solution of silver nitrate containing about 5 grams of the salt in 100 cc. water, add a few drops of mercury, and let it stand. In a few days the silver will be deposited in the form of delicate crystals. The formation is called the "silver tree."

### EXPERIMENTS TO ACCOMPANY CHAPTER XXIX.

#### ZINC AND ITS SALTS.

**Experiment 225.**—Heat a small piece of zinc on charcoal in the oxidizing flame of the blow-pipe. The white fumes of zinc oxide (philosopher's wool) will be seen, and the charcoal will be covered with a film which is yellow while hot, but becomes white on cooling.

**Experiment 226.**—Dissolve some zinc dust in a solution of sodium hydroxide, and see whether hydrogen is given off.

#### MERCURY AND ITS SALTS.

**Experiment 227.**—Make a solution of mercurous nitrate by treating at the ordinary temperature an excess of mercury with nitric acid, which is not too concentrated ; and with this solution study the conduct of mercurous salts.

**Experiment 228.**—Heat some of the solution of mercurous nitrate to boiling, then add a few drops of concentrated nitric acid, and boil again. With the solution thus obtained study the conduct of mercuric salts.

### EXPERIMENTS TO ACCOMPANY CHAPTER XXX.

#### TIN AND ITS COMPOUNDS.

**Experiment 229.**—Dissolve tin in hydrochloric acid and let the product crystallize.

**Experiment 230.**—Pass dry chlorine over granulated tin contained in a retort connected with a receiver, using the arrangement illustrated in Fig. 64, page 800. Redistil the product. Treat some of the liquid with water, and boil.

## Lead and its Compounds.

**Experiment 231.**—Make specimens of lead chloride and lead iodide, and crystallize them from water.

**Experiment 232.**—Make lead sesquioxide by bringing together lead acetate and sodium hydroxide, and treating the solution with a solution of sodium hypochlorite.

**Experiment 233.**—Treat some red lead with dilute nitric acid. Filter, wash, and treat the substance left on the filter with hydrochloric acid.

## EXPERIMENTS TO ACCOMPANY CHAPTER XXXI.

### Chromic Acid and the Chromates.

**Experiment 234.**—Powder some chromic iron very finely. Add 3 grams to a molten mixture of 3 grams each of potassium carbonate, potassium hydroxide, and potassium nitrate, heated in a porcelain crucible. After cooling treat the mass with water. Potassium chromate is in the solution.

**Experiment 235.**—To the solution of potassium chromate obtained in the last experiment add nitric acid to decompose the unacted-upon potassium carbonate, and give the solution an acid reaction. The color will change from yellow to red. The red color indicates the presence of the dichromate.

**Experiment 236.**—Treat a solution of 10 to 20 grams potassium dichromate with potassium hydroxide until the color becomes pure yellow, and evaporate to crystallization.

**Experiment 237.**—Make a solution of potassium dichromate saturated at the ordinary temperature. Pour into this $1\frac{1}{2}$ times its volume of ordinary concentrated sulphuric acid. After the liquid cools, and the chromium trioxide separates, filter with the aid of a filter-pump through glass-wool.

**Experiment 238.**—To a solution of potassium dichromate add some hydrochloric acid and a little alcohol. On boiling, the alcohol is oxidized, and the solution now contains chromic chloride.

### EXPERIMENTS TO ACCOMPANY CHAPTER XXXII.

#### Manganese and its Compounds.

**Experiment 239.**—Make and crystallize some manganous chloride by treating manganese dioxide with hydrochloric acid. Also make some manganous sulphate by heating manganese dioxide with sulphuric acid. Use these solutions for the purpose of studying the conduct of manganous salts.

**Experiment 240.**—In a small porcelain crucible heat together 5 grams manganese dioxide, 5 grams solid potassium hydroxide, and $2\frac{1}{2}$ grams potassium chlorate. When the mass has turned green, dissolve the contents in water and neutralize most of the free alkali in the solution. Or pass carbon dioxide through the solution without boiling.

### EXPERIMENTS TO ACCOMPANY CHAPTER XXXIII.

#### Iron and its Compounds.

**Experiment 241.**—Make ferric chloride by heating the purest iron wire in a current of chlorine. Also make a solution by dissolving iron in hydrochloric acid, and oxidizing the solution with nitric acid.

**Experiment 242.**—Make ferrous sulphate by dissolving iron in dilute sulphuric acid, and evaporating to crystallization. Dissolve equivalent quantities of ferrous sulphate and ammonium sulphate, and evaporate to crystallization.

**Experiment 243.**—Dissolve ferric hydroxide in sulphuric acid, and evaporate to dryness.

### EXPERIMENTS TO ACCOMPANY CHAPTER XXXIV.

#### Platinum.

**Experiment 244.**—Prepare a solution of platinic chloride as follows : Heat platinum in a flask with concentrated nitric acid, adding from time to time a few drops of hydrochloric acid. After the metal is dissolved evaporate to dryness. Dissolve in water and filter.

### Conclusion.

At the end of each chapter treating of the metallic or base-forming elements there is given a list of such reactions as are

of special value for analytical purposes, together with such explanatory statements as seem called for.  The student who is engaged in analytical work will generally find these explanations sufficient to enable him to keep his ideas clear in regard to the reactions with which he is dealing, provided, at the same time, he carefully studies the chapter to which the explanations form an appendix.  As an introduction to analytical work, a general study of chemical reactions is necessary, and the fuller this is the better.  There are many small books in existence in which good directions are given for work of this kind.  The student is, however, advised to supplement the book he may be using by such experiments as may suggest themselves on reading the corresponding chapters in this book.  The directions there found will generally be quite sufficient for the purpose, and it is therefore not considered necessary to give more specific directions in this place.  In general, the more the student occupies himself in the laboratory with chemical substances the more rapidly will his chemical ideas grow.  But it is necessary that he should avoid working by "rule of thumb," and for this purpose constant reference to some larger text-book in which the relations between the substances and the reactions he is dealing with are discussed in a broad way is of the highest importance.

# APPENDIX II.

THE following tables have been prepared to furnish those who may use this book as a reference-book in connection with laboratory work with such information as they may need, but which they can perhaps get only from works not always easily available. It was not considered advisable to include tables required in gas analysis and general quantitative analysis. For part of the material I am indebted to that excellent work, the Chemiker-Kalender, by R. Biedermann. In the tables of solubilities the substances have been arranged alphabetically as salts of acids, as for example the acetates, chlorides, sulphates, and sulphydrates.

J. ELLIOTT GILPIN.

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## ATOMIC WEIGHTS.

(From "The Constants of Nature," by F. W. Clarke, 1897.)

| | H = 1 | O = 16 | | H = 1 | O = 16 |
|---|---|---|---|---|---|
| Aluminium...... | 26.91 | 27.11 | Molybdenum.... | 95.26 | 95.99 |
| Antimony....... | 119.52 | 120.43 | Neodymium..... | 139.70 | 140.80 |
| Argon.... ..... | ? | ? | Nickel......... | 58.24 | 58.69 |
| Arsenic......... | 74.44 | 75.01 | Nitrogen........ | 13.93 | 14.04 |
| Barium......... | 136.39 | 137 43 | Osmium......... | 189.55 | 190.99 |
| Bismuth........ | 206 54 | 208.11 | Oxygen.... .... | 15.88 | 16 00 |
| Boron.... ...... | 10.86 | 10.95 | Palladium....... | 105.56 | 106.36 |
| Bromine........ | 79.34 | 79.95 | Phosphorus..... | 30.79 | 31.02 |
| Cadmium....... | 111 10 | 111.95 | Platinum........ | 193.41 | 194.89 |
| Cæsium......... | 131.89 | 132.89 | Potassium ....... | 38.82 | 39.11 |
| Calcium........ | 39.76 | 40.07 | Praseodymium... | 142.50 | 143.60 |
| Carbon......... | 11.92 | 12.01 | Rhodium........ | 102.23 | 103.01 |
| Cerium......... | 139.10 | 140.20 | Rubidium....... | 84 78 | 85.43 |
| Chlorine........ | 35.18 | 35.45 | Ruthenium...... | 100.91 | 101.68 |
| Chromium...... | 51.74 | 52.14 | Samarium........ | 149 13 | 150 26 |
| Cobalt.... ..... | 58.49 | 58.93 | Scandium....... | 43.78 | 44.12 |
| Columbium..... | 93.02 | 93.73 | Selenium........ | 78.42 | 79.02 |
| Copper.......... | 63.12 | 63.60 | Silicon ......... | 28.18 | 28.40 |
| Erbium......... | 165.06 | 166.32 | Silver.......... | 107.11 | 107.92 |
| Fluorine........ | 18.91 | 19.06 | Sodium.... ..... | 22.88 | 23.05 |
| Gadolinium...... | 155.57 | 156.76 | Strontium....... | 86.95 | 87.61 |
| Gallium......... | 69.38 | 69.91 | Sulphur......... | 31.83 | 32.07 |
| Germanium...... | 71.93 | 72.48 | Tantalum....... | 181.45 | 182.84 |
| Glucinum....... | 9.01 | 9.08 | Tellurium....... | 126.52 | 127.49 |
| Gold.... ....... | 195.74 | 197.23 | Terbium ........ | 158.80 | 160.00 |
| Helium.......... | ? | ? | Thallium........ | 202.61 | 204.15 |
| Hydrogen....... | 1.000 | 1.008 | Thorium........ | 230.87 | 232.63 |
| Indium.... .... | 112.99 | 113.85 | Thulium........ | 169.40 | 170.70 |
| Iodine.... ..... | 125.89 | 126.85 | Tin............. | 118.15 | 119.05 |
| Iridium......... | 191.66 | 193.12 | Titanium........ | 47.79 | 48.15 |
| Iron............ | 55.60 | 56.02 | Tungsten ....... | 183.43 | 184.83 |
| Lanthanum...... | 137.59 | 138.14 | Uranium........ | 237.77 | 239.59 |
| Lead........... | 205.36 | 206.92 | Vanadium....... | 50.99 | 51.38 |
| Lithium......... | 6.97 | 7.03 | Ytterbium....... | 171.88 | 173.19 |
| Magnesium...... | 24.10 | 24.28 | Yttrium ........ | 88.35 | 89.02 |
| Manganese...... | 54.57 | 54.99 | Zinc............ | 64.91 | 65.41 |
| Mercury........ | 198.49 | 200.00 | Zirconium....... | 89.72 | 90.40 |

## MELTING-POINTS AND BOILING POINTS OF THE ELEMENTS.

Where the values of different observers vary, the highest and lowest will be given.

| | Melting-point. | Boiling-point. |
|---|---|---|
| Aluminium...... | 600–850 | n.v. at white heat |
| Antimony....... | 425–450 | 1090–1700 |
| Argon ......... | − 189.6 | − 186.9 |
| Arsenic ........ | under pressure at red heat | sublimes at 450 |
| Barium ........ | red heat | |
| Beryllium...... | below 1000 | |
| Bismuth........ | 260–270 | 1090–1450 |
| Boron.......... | | |
| Bromine........ | − 7.3 | 59–63 |
| Cadmium....... | 310–320 | 760–860 |
| Cæsium........ | 26.5 | |
| Calcium........ | red heat | n.v. |
| Carbon......... | infusible | |
| Cerium......... | between Sb and Ag | |
| Chlorine ....... | solidifies at − 102 | − 33.6 |
| Chromium...... | higher than platinum | |
| Cobalt......... | 1500–1800 | |
| Copper......... | 1000–1330 | |
| Fluorine....... | | |
| Gallium........ | 30.15 | |
| Germanium..... | about 900 | |
| Gold........... | 1035–1250 | |
| Indium ........ | 176 | red heat |
| Iodine......... | 113–115 | above 200 |
| Iridium........ | 1950–2500 | |
| Iron, pure...... | 1500–1800 | |
| Lead........... | 322–335 | between 1450–1600 |
| Lithium........ | 180 | |
| Magnesium .... | 500–800 | about 1100 |
| Manganese..... | 1600 | |
| Mercury........ | − 38.50 to − 40.5 | 357.25 |
| Molybdenum.... | does not melt at a white heat | |
| Nickel......... | 1450–1600 | |
| Nitrogen....... | solidifies at − 203 at 60–70 mm. | − 194 4 |
| Osmium ....... | 2500 | |
| Oxygen........ | below − 211.5 at 9 mm. | − 181.4 |
| Palladium ..... | 1360–1950 | |
| Phosphorus..... | 44.2 | 287–290 |
| Platinum....... | 1460–2200 | |
| Potassium...... | 58–62.5 | 667–731 |
| Rhodium....... | 2000 | |
| Rubidium...... | 38.5 | |
| Selenium....... | 217 | bet. 676 and 683 |
| Silicon........ | about 1400 | |
| Silver......... | 954–1040 | |
| Sodium........ | 90–97.6 | 742–954 |
| Strontium..... | red heat | |
| Sulphur, rhombic. | 113–115 | 447–448.4 |
| "      mono... | 120 | |
| "      amor.... | above 120 | |
| Tellurium...... | 425–525 | |
| Tin............ | 226.5–235 | bet. 1450 and 1600 |
| Zinc.......... | 412–420 | 891–1040 |

## MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES.

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| **ACETATES :** | | | | | | | |
| Lead acetate.......... | $Pb(C_2H_3O_2)_2 + 3H_2O$ | ...... | 200 | ........... | 2 : 3 | 2 : 1 | sol. |
| Sodium acetate ...... | $NaC_2H_3O_2 + 3H_2O$ | ...... | 319 | ........... | 33 | 200 | sol. Al. |
| Uranyl acetate........ | $(UO_2)(C_2H_3O_2)_2+2H_2O$ | ...... | W. H. | ........... | sol. | sol. | sol. |
| **ACIDS :** | | | | | | | |
| Arsenic acid.......... | $H_3AsO_4 + H_2O$ | ...... | 200 | ........... | 16.7 | 50 | sol. Alk. |
| Boric acid ........... | $H_3BoO_3$ | VI | 184–186 | ........... | 4 | 34 | 1–6 Al. |
| Chloric acid.......... | $HClO_3 (+ 7H_2O)$ | ...... | decomp. | decomp. | sol. | ........ | ...... |
| Hydriodic acid ....... | HI | ...... | – 55 | 0° at 4 atm. | very sol. | ........ | sol. Al. |
| " " hydride. | $HCl$ | ...... | ........ | 40 atm. 10° | 525 : 1 vol. | ........ | ...... |
| " " | $HCl + H_2O(45.2\%)$ | ...... | ........ | ........... | ∞ | ........ | ∞ Al. |
| " " | $HCl + 8H_2O(20.18\%)$ | ...... | ........ | ........... | ∞ | ........ | ∞ Al. |
| Hydrobromic acid.... | HBr | ...... | – 120 | 110 | very sol. | sol. | sol. Al. |
| Hydrocyanic acid.... | HCN | ...... | – 13.8 | – 69 | ∞ | ∞ | ∞ Al. |
| Hypophosphorous acid.. | $H_3PO_2$ | ...... | 17.4 | 26.5 | ........ | very sol. | ...... |
| Metaphosphoric acid...... | $HPO_3$ | ...... | ........ | decomp. W. H. | sol. | sol. | ...... |
| Metastannic acid...... | $H_2SnO_3$ | ...... | ........ | ........... | very little sol | very little sol | { sol. Alk., sol. HCl |
| Metavanadic acid...... | $HVO_3$ | ...... | ........ | ........... | sol. | sol. | ...... |
| Nitric acid........... | $HNO_3$ | ...... | – 50 | 86 w. decom. | ∞ | ∞ | ...... |
| Perchloric acid....... | $HClO_4$ | ...... | ........ | explodes 110 | sol. | sol. | decomp. Al. |
| Phosphoric acid...... | $H_3PO_4$ | IV | liquid – 35 / 40.5 | decomp. 213 | very so ] | very sol. | ...... |

Note.—In this table the following abbreviations have been used: W. H. = white heat; R. H. = read heat; h. = hot; f. p. = freshly precipitated; Al. = Alcohol; Alk. = Alkali; Ac. = Acid. Crystal System: I, regular; II, tetragonal; III, hexagonal; IIIa, rhombo-hedral; IV, orthorhombic; V, monoclinic; VI, triclinic.

MELTING-POINTS, BOILING POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| ACIDS (cont'd): | | | | | | | |
| Phosphorous acid | $H_3PO_3$ | ..... | 70 | decomp. 200 | very sol. | very sol. | ......... |
| Silicic acid | $H_2SiO_3$ | ..... | ..... | ..... | 0.0129 f. p. : 1 | insol. | sol. Alk. |
| Sulphuric acid, conc. | $H_2SO_4$ (98.5%) | ..... | ..... | ..... | $\infty$ | $\infty$ | decomp. Al. |
| " " English | $H_2SO_4$ (92%) | ..... | + 8 | 210–338 | $\infty$ | $\infty$ | " " |
| " " hydrate | $H_2SO_4 + H_2O$ | ..... | ..... | 170–190 | $\infty$ | $\infty$ | " " |
| " " " | $H_2SO_4 + 2H_2O$ | ..... | 10.5 | decomp. 40 | $\infty$ | $\infty$ | " " |
| " " water-free | $H_2SO_4$ | ..... | ..... | ..... | sol. | ......... | HCl decomp. |
| Telluric acid | $H_2TeO_4 + 2H_2O$ | III | R. H decom. | 160 | s. sol. | ......... | s. sol. Al. |
| ANTIMONIATE: Sodium pyro-antimoniate | $Na_2H_2Sb_2O_7 + 6H_2O$ | ..... | ..... | ..... | s. sol. | s. sol. | s. sol. Al. |
| ARSENATE: Ammonium magnesium arsenate | $Mg(NH_4)AsO_4 + H_2O$ | ..... | ..... | ..... | 0.02 | insol. | insol. Al. |
| BORATE: Sodium borate, Borax | $Na_2B_4O_7 + 10H_2O$ | V | R. H. | ..... | 6 | 200 | insol. Al. |
| BROMIDES: | | | | | | | |
| Lead bromide | $PbBr_2$ | ..... | low R. | ..... | s. sol. | more sol. | insol. Al. |
| Phosphorus pentabromide | $PBr_5$ | ..... | below 100 | 100 | decomp. | decomp. | decomp. |
| Potassium bromide | $KBr$ | I | R. H. | ..... | 25 | 100 | Al 0.5 : h 6.215 |
| Silver bromide | $AgBr$ | I | about 430 | 700 decomp. | insol. | insol. | sol. con. $NH_3$ & con. HBr |
| Sodium bromide | $NaBr + 4H_2O$ | ..... | ..... | ..... | 75 | 112 | s. sol. Al. |
| CARBONATES: | | | | | | | |
| Ammonium carbonate | $(NH_4)_2CO_3 + H_2O$ | ..... | ..... | ..... | sol. | sol. | ......... |
| Barium carbonate | $BaCO_3$ | IV | ..... | ..... | insol. | insol. | insol. Al. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling Point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| CARBONATES (cont'd): | | | | | | | |
| Calcium carbonate...... | $CaCO_3$ | IIIa or IV | { decomp. R. H. | ......... | 0.0018 | 0.088 | { water containing $CO_2$ insol. Al. |
| Lead carbonate........ | $PbCO_3$ | IV | ......... | ......... | 0.00198 | insol. | ......... |
| Magnesium carbonate.... | $MgCO_3$ | IIIa or IV | { decomp. | ......... | water containing $CO_2$ 0.1316 at 5° | | ......... |
| Potassium carbonate..... | $K_2CO_3 + 2H_2O$ | V | ......... | ......... | 1.1₁1 | very sol. | insol. Al. |
| Sodium carbonate...... | $Na_2CO_3 + 10H_2O$ | V | 34 | ......... | 21.33 | 420 | "  " |
| CHLORATES : | | | | | | | |
| Barium chlorate........ | $Ba(ClO_3)_2 + H_2O$ | V | ......... | decomp. | 25 | 125 | s. sol. Al. |
| Potassium chlorate...... | $KClO_3$ | V | 334 | ......... | 6.25 | 50 | Al. 0.883 |
| CHLORIDES : | | | | | | | |
| Aluminium chloride...... | $AlCl_3 + 6H_2O$ | ...... | { 190 (pres. 2.5 atm) | 180 | 400 | very sol. | 50 Al. |
| Ammonium chloride...... | $NH_4Cl$ | I or II | ......... | 350 diss. | 33/10° | 77/100° | 12/8° Al. Al 0.005 |
| "  platinum chloride | $(NH_4)_2PtCl_6$ | ...... | ......... | ......... | 0.67 | 1.25 | { sol. con. HCl & Al. |
| Antimony trichloride. ... | $SbCl_3$ | ...... | 72 | 230 | { sol. much decomp. | { decomp. | ......... |
| "  pentachloride .. | $SbCl_5$ | ...... | − 6 | decomp. | decomp. | " | ......... |
| Arsenic trichloride....... | $AsCl_3$ | ...... | vol. − 29 | 134 | sol. decomp. | " | sol. HCl, sol. |
| Auric chloride......... | $AuCl_3 + 2H_2O$ | ...... | decomp. | ......... | sol. | sol. | sol. Al. [Al. |
| Aurous chloride........ | $AuCl$ | ...... | ......... | ......... | decomp. | decomp. | ......... |
| Barium chloride....... | $BaCl_2 + 2H_2O$ | IV | { $2H_2O$ 113° R. H. | ......... | 33.4/10° | 60/104° | { insol. Al., s. sol. HCl and $HNO_3$ |
| Bismuth chloride....... | $BiCl_3$ | ...... | 230 | ......... | decomp. | decomp. | sol. HCl |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—*(Continued)*.

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. Cold Water. | Hot Water. | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| **CHLORIDES** *(cont'd)*: | | | | | | | |
| Cadmium chloride.......... | $CdCl_2 + 2H_2O$ | ...... | ...... | $\{4H_2O$ at $30$ | 140 | 150 | sol. Alk. |
| Calcium chloride.......... | $CaCl_2 + 6H_2O$ | III | 728 | $6H_2O$ at $200$ / sublim. W.H. | 400 | 650 | 13 Al. |
| Chromic chloride.......... | $CrCl_3$ | ...... | ...... | ...... | insol. | insol. | insol. Al. |
| Chromous chloride......... | $CrCl_2$ | ...... | ...... | ...... | sol. | sol. | ...... |
| Cobaltous chloride........ | $CoCl_2 + 6H_2O$ | ...... | 86.75 | $6H_2O$ at $140$ | " | " | ...... |
| Cuprous chloride.......... | $CuCl$ | ...... | 410 | ...... | s. sol. | ...... | $\{$sol. in HCl and NH₃ |
| Cupric chloride........... | $CuCl_2 + 2H_2O$ | IV | ...... | decomp. R.H. | 121.4/16.1° | very sol. | sol. Al. |
| Ferric chloride........... | $FeCl_3$ | III | ...... | 280–285 | decomp. | " | " |
| Ferrous chloride.......... | $FeCl_2 + 4H_2O$ | V | R.H. | ...... | 130 | " | " |
| Lead chloride............ | $PbCl_2$ | IV | ...... | ...... | 0.74 | 5 | sol. Al. 0.5 |
| Magnesium chloride........ | $MgCl_2 + 6H_2O$ | ...... | R.H. | ...... | 130 | 367 | Al. 50 |
| Manganous chloride........ | $MnCl_2 + 4H_2O$ | V | ...... | ...... | 150 | 650 | Al. 53 |
| Mercuric chloride ........ | $HgCl_2$ | IV | 260–270 | 300 | 7 | 54 | $\{$33 Al. / 25 Ether |
| Mercurous chloride ....... | $HgCl$ | IV | ...... | diss. | insol. | insol. | insol. Al. |
| Phosphorus pentachloride.. | $PCl_5$ | ...... | 148 | $\{$sub. below 100 | decomp. | decomp. | $\{$decomp. / insol. CS₂ |
| " trichloride... | $PCl_3$ | V | decomp. | 78.3 | " | " | sol. CS₂ |
| Platinum chloride......... | $PtCl_4 + 8H_2O$ | I | R.H. | sub. W. H. | sol. | very sol. | sol. Al. |
| Potassium chloride........ | $KCl$ | I | decomp. | ...... | 1 | 5.26 | 8.27 Al. |
| " chlorplatinate... | $K_2PtCl_6$ | ...... | sub. | ...... | decomp. | ...... | sol. POCl₃ |
| Selenium tetrachloride.... | $SeCl_4$ | ...... | ...... | ...... | ...... | ...... | ...... |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| **CHLORIDES** (cont'd): | | | | | | | |
| Silicon chloroform...... | $SiHCl_3$ | ...... | ...... | 36 | decomp. | ...... | ...... |
| Silicon tetrachloride...... | $SiCl_4$ | I | ...... | 59 | insol. | insol. | sol. $NH_3$, KCN, conc. HCl, $Na_2S_2O_3$ insol. Al. |
| Silver chloride...... | $AgCl$ | I | 260 | ...... | 35 | 39.5 | sol. Al. |
| Sodium chloride......... | $NaCl$ | I | 772–776 | ...... | very sol. 44/0° | very sol. 117/118° | 4.6 Al. |
| Sodium chlorplatinate.... | $Na_2PtCl_6 + 6H_2O$ | ...... | ...... | ...... | sol. de comp. by much water | comp. by water | sol. $CS_2$ |
| Stannic chloride......... | $SnCl_4$ | ...... | ...... | 120 | much | decomp. by much water | } sol. Al. |
| Stannous chloride...... | $SnCl_2 + 2H_2O$ | ...... | 250 | 606 | 271 | | |
| Strontium chloride........ | $SrCl_2 + 6H_2O$ | III | 829 $H_2O$ free | ...... | } slowly decomp. | decomp. | ...... |
| Sulphur chloride......... | $S_2Cl_2$ | ...... | ...... | 138 | decomp. | decomp. | ...... |
| dichloride......... | $SCl_2$ | ...... | ...... | decomp. | | | ...... |
| Thallium chloride........ | $TlCl_3 + H_2O$ | ...... | decomp. 100 | 346 | very sol. | decomp. | sol. $CS_2$ |
| Tungsten hexachloride.... | $WCl_6$ | ...... | 275 | vol. | decomp. 60° | | ...... |
| Uranium chloride..... | $UCl_4$ | ...... | ...... | 154 | sol. | sol. | ...... |
| Vanadium chloride....... | $VCl_4$ | ...... | – 18 vol. | above 400 | sol. decomp. | | Al. 1 : 1 |
| Zinc chloride........... | $ZnCl_2$ | ...... | 250 | ...... | 300 | very sol. | ...... |
| **CHROMATES:** | | | | | | | |
| Ammonium bichromate... | $(NH_4)_2Cr_2O_7$ | V | forms $Cr_2O_3$ | ...... | very sol. | very sol. | ...... |
| Barium chromate......... | $BaCrO_4$ | | ...... | ...... | insol. | insol. | sol. Alk. |
| Lead chromate.......... | $PbCrO_4$ | V | fuses | ...... | insol. | insol. | ...... |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| CHROMATES (cont'd): | | | | | | | |
| Potassium chromate | $K_2CrO_4$ | IV | R. H. | .......... | 50 | 60 | insol. Al. |
| Sodium chromate | $Na_2CrO_4 + 10H_2O$ | V | .......... | .......... | sol. | sol. | .......... |
| CYANIDES: | | | | | | | |
| Cobalt cyanide | $Co(CN)_2 + 3H_2O$ | ...... | dehyd. at 250 | .......... | insol. | .......... | sol. in KCN Al. 2⅓ vols. |
| Cyanogen | $(CN)_2$ | ...... | − 34 | − 21 | 4.5 : 1 vol. | .......... | s. sol. Al. |
| Potassium cyanide | KCN | I | R. H. | .......... | very sol. | decomp. | insol. Al. |
| " ferricyanide | $K_3Fe(CN)_6$ | V | .......... | .......... | 40 | 80 | insol. Al. |
| " ferrocyanide | $K_4Fe(CN)_6 + 3H_2O$ | II | .......... | .......... | 28 | 100 | insol. Al. |
| FLUORIDES: | | | | | | | |
| Calcium fluoride | $CaFl_2$ | ...... | .......... | .......... | 0.05 | s. sol. | sol. in $H_2O$ contain g$CO_2$ |
| Potassium silicofluoride | $K_2SiF_6$ | I | decom. R. H. | .......... | 0 12 | 2 | insol. Al. |
| Silicon fluoride | $SiF_4$ | ...... | − 140 | −107 | decomp. | .......... | .......... |
| HYDRIDES: | | | | | | | |
| Ammonia | $NH_3$ | ...... | − 75 | − 35 | 1050 | 97 vols. 100° | sol. Al. |
| Arsine | $AsH_3$ | ...... | gas | − 40 | 5.1 vol. | insol. | .......... |
| Phosphine | $PH_3$ | ...... | − 313 | − 85 | s. sol. | insol. | .......... |
| Stibine | $SbH_3$ | ...... | − 91.5 | − 18 | .......... | 4 | .......... |
| HYDROXIDES: | | | | | | | |
| Aluminium hydroxide | $Al(OH)_3$ | ...... | decom. at 300 | .......... | insol. | insol. | sol. in acids and alkalies |
| Barium hydroxide | $Ba(OH)_2 + 8H_2O$ | II { 7 $H_2O$ in air 1 at R. H. } | .......... | 1.7/0° | 101/80° | s. sol. Al. |
| Calcium hydroxide | $Ca(OH)_2$ | ...... | .......... | .......... | .137/20° | .06/100° | insol. Al. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| HYDROXIDES (cont'd): | | | | | | | |
| Chromium hydroxide...... | $Cr(OH)_3 + 4H_2O$ | ...... | 4H₂O at 100 | ...... | insol. | insol. | { sol. in Ac. and Alk. |
| Copper hydroxide.......... | $Cu(OH)_2$ | ...... | decomp. | ...... | " | " | sol. NH₃ |
| Ferric hydroxide........... | $Fe(OH)_3$ | ...... | ...... | ...... | " | " | insol. Al. |
| Ferrous hydroxide......... | $Fe(OH)_2$ | ...... | ...... | ...... | s. sol. | ...... | ...... |
| Lead hydroxide........... | $Pb(OH)_2$ | ...... | decomp. 145 | ...... | " | s. sol. | sol. Alk. |
| Magnesium hydroxide...... | $Mg(OH)_2$ | ...... | decomp. | ...... | insol. | insol. | sol. in NH₄Cl |
| Nickelic hydroxide........ | $Ni(OH)_3$ | ...... | ...... | ...... | " | " | { sol. in Ac. and NH₃ |
| Nickelous hydroxide....... | $Ni(OH)_2$ | ...... | ...... | ...... | " | " | sol. in NH₃ |
| Potassium hydroxide....... | KOH | ...... | R. H. | ...... | 200 | very sol. 210 | sol. Al. |
| Sodium hydroxide ........ | NaOH | ...... | below R. H. | ...... | 60 | 4/100° | " |
| Strontium hydroxide....... | $Sr(OH)_2 + 8H_2O$ | II | ...... | ...... | 2/10³ | ...... | ...... |
| Zinc hydroxide............ | $Zn(OH)_2$ | IV | decomp. | ...... | insol. | insol. | { sol. Ac. and Alk. |
| HYPOCHLORITES: | | | | | | | |
| Calcium hypochlorite..... | $CaOCl_2$ | ...... | decomp. | ...... | s. sol. | ...... | decomp. Al. |
| Potassium hypochlorite ... | KClO | ...... | ...... | ...... | very sol. | very sol. | ...... |
| IODIDES : | | | | | | | |
| Mercuric iodide .......... | $HgI_2$ | IV | 238 | ...... | 2 | s. sol. | 0.8 Al. |
| Phosphonium iodide...... | $PH_4I$ | II | sub. | about 80 | decomp. | decomp | decomp. |
| Potassium iodide. ........ | KI | I | ...... | ...... | 120 | 200 | Al. 14 28 |
| Silver iodide............. | AgI | III | R. H. | ...... | insol. | ...... | s. sol. NH₃ |
| MANGANATE : | | | | | | | |
| Potassium manganate. ... | $K_2MnO_4$ | IV | ...... | ...... | sol. | decomp. | sol. Alk. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. Cold Water. | Solubility in 100 Parts. Hot Water. | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| NITRATES : | | | | | | | |
| Barium nitrate......... | Ba(NO₃)₂ | I | ...... | ...... | 5.2/0° | 34.8/102° | insol. Al. |
| Bismuth nitrate........ | Bi(NO₃)₃ + 5H₂O | VI | decomp. R.H. | 5H₂O at 80 | decomp. | decomp. | sol. HNO₃ |
| Cobalt nitrate......... | Co(NO₃)₂ + 6H₂O | V | 73 | decomp. | very sol. | very sol. | 200 Al. |
| Copper nitrate......... | Cu(NO₃)₂ + 6H₂O | I | ...... | ...... | | | very sol. |
| Lead nitrate........... | Pb(NO₃)₂ | I | decomp. R.H. | ...... | 48/10° | 139/100° | sol. Al. |
| Mercuric nitrate....... | Hg(NO₃)₂ | | decomp. R.H. | ...... | changed to basic salt | | sol. HNO₃ |
| Potassium nitrate...... | KNO₃ | IV & III a | 339 | decomp. | 25 | 200 | insol. Al. |
| Silver nitrate......... | AgNO₃ | IV | 198 | decomp. R.H. | 122 | 111 | Al. h. 1 : 4 |
| Uranyl nitrate......... | UO₂(NC₃)₂ + 6H₂O | | 59.5 | ...... | 200 | very sol. | very sol. Al. |
| NITROPRUSSIATE : | | | | | | | |
| Sodium nitroprussiate... | Na₂FeCn₅(NO) + 2H₂O | | | | 40 : 100 | very sol. | s. sol. |
| OXALATE : | | | | | | | |
| Ammonium oxalate....... | (NH₄)₂C₂O₄ | | | | very sol. | very sol. | ...... |
| OXIDES : | | | | | | | |
| Antimony trioxide...... | Sb₂O₃ | IV & I | ...... | sub. | insol. | ...... | sol. conc. HCl |
| Arsenic trioxide....... | As₂O₃ | | sub. | ...... | 4 | ...... | sol. HCl |
| Barium superoxide...... | BaO₂ | | R. H. | ...... | insol. | ...... | `` |
| Barium superoxide hydrate | BaO₂ + 8H₂O | | 6H₂O at 130 | ...... | s. sol. | 9.5 | ...... |
| Boric acid anhydride.... | Bo₂O₃ | | R. H. | ...... | 3 | decomp. | sol. Al. |
| Calcium oxide.......... | CaO | | ...... | ...... | 0.12 | 0.078 | sol. in H₂O cont'g CO₂ |
| Carbon dioxide......... | CO₂ | | − 70 | 0° at 36 atm. | 1 : 1 | ...... | ...... |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal Sys-tem. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| OXIDES (cont'd): | | | | | | | |
| Carbon monoxide.......... | CO | ...... | ........ | ........ | 1 : 30 | ........ | } sol. in NH₃ or acid CuCl |
| Chromic oxide............ | Cr₂O₃ | III | W. H. | ........ | insol. | insol. | insol. Al. |
| Cupric oxide............. | CuO | I & V | ........ | ........ | " | " | " |
| Cuprous oxide........... | Cu₂O | I | ........ | ........ | " | " | sol. NH₃ |
| Ferric oxide............ | Fe₂O₃ | IIIa | ........ | ........ | " | " | sol. Ac. |
| Ferrous oxide........... | FeO | I | ........ | ........ | " | " | " |
| Ferrous-ferric oxide..... | Fe₃O₄ | ...... | ........ | ........ | " | " | insol. Al. |
| Hydrogen peroxide....... | H₂O₂ | ...... | vol. | decomp. | ∞ | ........ | ........ |
| Lead sesquioxide......... | Pb₂O₃ | ...... | decomp. | ........ | insol. | insol. | insol. Alk. |
| Lead suboxide........... | Pb₂O | ...... | " | ........ | decomp. | decomp. | decom. Alk. |
| Lead superoxide......... | PbO₂ | ...... | " | ........ | insol. | insol. | insol. Al. |
| Manganese dioxide....... | MnO₂ | II | ........ | ........ | " | " | sol. Ac. |
| Manganous oxide........ | MnO | ...... | ........ | ........ | " | " | " |
| Manganous-manganicoxide | Mn₃O₄ | ...... | W. H. | ........ | " | " | insol. Al. |
| Mercuric oxide.......... | HgO | ...... | decom. R. H. | ........ | s. sol. | s. sol. | } sol. in FeSO₄ solution |
| Nitric oxide............ | NO | ...... | − 167 | − 153.6 | 1 : 20 vols. | ........ | ........ |
| Nitrogen peroxide........ | NO₂ | ...... | − 11.5 | 26 | decomp. | decomp. | ........ |
| Nitrous oxide........... | N₂O | ...... | − 99 | − 92 | 1.3 : 1 vol. | s. sol. | ........ |
| Osmium tetroxide....... | OsO₄ | V | 20 | 100 | sol. | sol. | } sol. Alk., sol. Al. |
| Phosphorus pentoxide.... | P₂O₅ | ...... | subl. | ........ | ........ | decomp. | ........ |
| Silicon dioxide.......... | SiO₂ | ...... | ........ | ........ | insol. | insol. | insol. Al. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| OXIDES (cont'd): | | | | | | | |
| Silver oxide ............ | $Ag_2O$ | .... | decomp. 250 | ...... | 0.333 | ........ | sol. $HNO_3$ |
| Sulphur dioxide ........ | $SO_2$ | .... | −79 | −8 | 688 vol. at 0° | 170 vol. at 40° | ........ |
| "   trioxide.......... | $SO_3$ | .... | 14.8 | 46 | decomp. | decomp. | decomp. |
| Stannic oxide........... | $SnO_2$ | II | ........ | .. ...... | insol. | ........ | sol. Alk., $H_2SO_4$ insol. Ac. |
| Zinc oxide............. | $ZnO$ | .... | ........ | ........ | 1 : 100000 | ........ | sol. Ac. |
| OXYCHLORIDES: | | | | | | | |
| Antimony oxychloride.... | $SbOCl$ | .... | decomp. | decomp. | insol. | insol. | insol.Alk., sol. HCl |
| Phosphorus oxychloride... | $POCl_3$ | .... | −1.5 | 110 | decomp. | decomp. | decomp. |
| PERCHLORATE: | | | | | | | |
| Potassium perchlorate.... | $KClO_4$ | IV | decomp. | ........ | 1.66 | 18.18 | insol. Al. |
| PERIODATE: | | | | | | | |
| Potassium periodate....... | $KIO_4$ | IV | decomp. | ........ | 0.34 | sol. | ........ |
| PERMANGANATE: | | | | | | | |
| Potassium permanganate .. | $KMnO_4$ | IV | decomp. | ........ | 6.451 | very sol. | decomp. |
| PHOSPHATES: | | | | | | | |
| Ammonium   magnesium phosphate........... | $Mg(NH_4)PO_4 + 6H_2O$ | II | ........ | ........ | 0.005 | insol. | insol. Al. |
| Calcium phosphate, prim... | $CaH_4(PO_4)_2 + H_2O$ | IV | ........ | ........ | decomp. | decomp. | ........ |
| "    "    second | $CaHPO_4 + 2H_2O$ | .... | ........ | ........ | insol. | insol. | sol. Ac. |
| "    "    tertiary | $Ca_3(PO_4)_2$ | .... | ........ | ........ | " | " | " " |
| Magnesium pyrophosphate. | $Mg_2P_2O_7 + 5H_2O$ | .... | ........ | ........ | " | " | insol. Al. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| **PHOSPHATES** (*cont'd*): | | | | | | | |
| Potassium pyrophosphate.. | $K_2P_2O_7 + 3H_2O$ | ...... | ...... | ...... | sol. | very sol. | ............ |
| Sodium hypophosphite.... | $NaH_2PO_2 + H_2O$ | ...... | $\{$ $H_2O$ 100, 180, 300 $\}$ | ...... | " | sol. | .......... |
| phosphate, meta.. | $NaPO_3$ | ...... | $H_2O$ in vac. decomp. R.H. | ...... | insol. | insol. | insol. Al. |
| " " normal | $Na_3PO_4 + 12H_2O$ | III | $\{$ $1H_2O$ at 80, $11H_2O$ at100, 76.7 $\}$ | ...... | 20 | sol. | .......... |
| " " pyro... | $Na_4P_2O_7 + 10H_2O$ | V | $H_2O$ at 60 | ...... | insol. | insol. | insol. Al. |
| Uranyl phosphate......... | $UO_2(HPO_4)_2 + 4H_2O$ | ...... | ...... | ...... | " | $\{$ " $\}$ | insol. Acetic Acid. |
| **PHOSPHOMOLYBDATE:** | | | | | | | |
| Ammonium phosphomolyb- date .............. | $\{$ $(NH_4)_3PO_4 + 10MoO_3 + 3H_2O$ $\}$ | ...... | ...... | ...... | " | " | insol. Al. |
| **SELENIDE:** | | | | | | | |
| Hydrogen selenide........ | $H_2Se$ | .... | diss. from 150–520 | ...... | very sol. | ...... | .......... |
| **SILICATES:** | | | | | | | |
| Potassium silicate........ | $K_2SiO_3$ | IV | ...... | ...... | sol. | sol. | .......... |
| Sodium silicate.......... | $Na_2SiO_3$ | IV | ...... | ...... | " | " | insol. Al. |
| **SULPHATES:** | | | | | | | |
| Aluminium sulphate........ | $Al_2(SO_4)_3 + 18H_2O$ | V | ...... | ...... | 85 | 1130 | s. sol. Al. |
| Ammonium sulphate...... | $(NH_4)_2SO_4$ | IV | 140 | decomp. | 76.8 | 87.8/100° | insol. Al. |
| Barium sulphate.......... | $BaSO_4$ | IV | ...... | ...... | insol. | insol. | sol. conc. $H_2SO_4$ at 100 |
| Cadmium sulphate........ | $3CdSO_4 + 8H_2O$ | V | ...... | ...... | 7·25/23° | very sol. | insol. Al. |
| Calcium sulphate. ....... | $CaSO_4 + 2H_2O$ | V | $2H_2O$ at 130 | ...... | 0.205/0° | 0.2174/100° | " |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. | | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| | | | | | Cold Water. | Hot Water. | |
| SULPHATES (cont'd): | | | | | | | |
| Chromium sulphate......... | $Cr_2(SO_4)_3 + 18H_2O$ | ...... | ............ | ............ | sol. | sol. green | sol. Al. green |
| Copper sulphate......... | $CuSO_4 + 5H_2O$ | VI | $4H_2O$ at 100, $5H_2O$ at 240 | decomp. R. H. | 40 | 203 | insol. Al. |
| Ferrous sulphate........... | $FeSO_4 + 7H_2O$ | V, IV / 5 aq. VI / 4 aq. II | $6H_2O$ at 140, $7H_2O$ at 280 | decomp. R. H. | 60 | 333 | insol. Ac. |
| Ferrous ammonium sulphate.................. | $Fe(NH_4)_2(SO_4)_2 + 6H_2O$ | V | ............ | ............ | 17 | very sol. | " |
| Lead sulphate............: | $PbSO_4$ | IV | R. H. | ............ | ............ | ............ | { insol. Al., sol. Alk. |
| Magnesium sulphate....... | $MgSO_4 + 7H_2O$ | IV & V | $5H_2O$ at 150, $7H_2O$ at 250 | ............ | 25 8/0° | 71.43 | sol. Al. |
| Potassium chrome-sulphate | $KCr(SO_4)_2 + 12H_2O$ | I | $11H_2O$ at 200, $12H_2O$ at 400 | ............ | 20 | 50 | insol. Al. |
| Potassium ferric sulphate.. | $KFe(SO_4)_2 + 12H_2O$ | I | decomp. R. H. | ............ | 20 | very sol. | ............ |
| Potassium pyrosulphate... | $K_2S_2O_7$ | ...... | ............ | ............ | ............ | 25 | insol. Al. |
| Potassium sulphate... ... | $K_2SO_4$ | IV | ............ | ............ | 12.5 | { 42.5 ($Na_2SO_4$) } | " |
| Sodium sulphate........... | $Na_2SO_4 + 10H_2O$ | V | $7H_2O$ at 150 | ............ | 5/0° | very sol. 655 | sol. $H_2SO_4$ |
| Uranyl sulphate........... | $UO_2SO_4 + 3H_2O$ | ...... | ............ | ............ | very sol. 135 | | insol. |
| Zinc sulphate............ | $ZnSO_4 + 7H_2O$ | IV | $6H_2O$ at 100 | ............ | sol. | sol. | ............ |
| SULPHYDRATES: | | | | | | | |
| Ammonium sulphydrate... | $NH_4HS$ | ...... | ............ | ............ | sol. | sol. | ............ |
| Potassium sulphydrate.... | $KHS$ | ...... | ............ | ............ | " | " | sol. |

MELTING-POINTS, BOILING-POINTS, AND SOLUBILITIES OF INORGANIC SUBSTANCES—(Continued).

| Name. | Formula. | Crystal System. | Melting-point, °C. | Boiling-point, °C. | Solubility in 100 Parts. Cold Water. | Hot Water. | Alcohol, Acids, Alkalies, and Other Solvents. |
|---|---|---|---|---|---|---|---|
| SULPHIDES : | | | | | | | |
| Arsenic sulphide............ | As₂S₃ | .... | melts W. H. | subl. | insol. | insol. | sol. Alk. |
| Cadmium sulphide.......... | CdS | III | ...... | ...... | " | " | sol. conc. Ac. ∞ Al. |
| Carbon disulphide.......... | CS₂ | .... | −116 | 46 | 2 : 1000/0° | 1.4:10000/50° | insol. Al. |
| Copper sulphide............ | CuS | .... | ...... | ...... | insol. | insol. | ...... |
| Hydrogen sulphide......... | H₂S | .... | −85 | −61.8 | 1 : 4.37 v. 0° | 3.23 v. 15° | sol. Ac. |
| Iron sulphide.............. | FeS | .... | R. H. | ...... | insol. | insol. | insol. Al. |
| Lead sulphide.............. | PbS | .... | " | subl. | " | " | insol. Al. |
| Mercuric sulphide.......... | HgS | IIIa | ...... | " | " | " | sol. aqua regia |
| Potassium sulphide ........ | K₂S | I | ...... | ...... | very sol. | very sol. | sol. Al. |
| Silver sulphide............ | Ag₂S | I | ...... | ...... | insol. | ...... | insol. NH₃ |
| Zinc sulphide.............. | ZnS | | ...... | ...... | " | insol. | insol. Al. |
| SULPHITES : | | | | | | | |
| Potassium sulphite......... | K₂SO₃ + 2H₂O | V | ...... | ...... | 100 | very sol. | insol. Al. |
| Sodium sulphite........... | Na₂SO₃ + 7H₂O | V | ...... | ...... | 25 | 100 | " |
| SULPHOCYANATES : | | | | | | | |
| Ammonium sulphocyanate | NH₄CNS | .... | 169 | 170 decomp. | sol. | very sol. | sol. Al. |
| Potassium sulphocyanate.. | KCNS | .... | ...... | ...... | very sol. | " | " Al. |
| TARTRATES : | | | | | | | |
| Potassium tartrate........ | K₂H₄C₄O₆ | .... | H₂O at 180 | ...... | 150 | ...... | Al. hot 0.4 |
| Potassium antimonyl tartrate.......... | K(SbO)C₄H₄O₆ + ½H₂O | .... | ½H₂O at 100 | ...... | 7 | 53 | insol. Al. |
| THIOSULPHATE : | | | | | | | |
| Sodium thiosulphate...... | Na₂S₂O₃ + 5H₂O | V | H₂O at 215 | decomp. 220 | 102 | very sol. | insol. Al. |

## WEIGHT OF 1 LITER OF GAS AT 0° AND 760 MM. PRESSURE IN LATITUDE 45°.

| Name. | Formulæ. | Molecular Weight. | Weight of 1 Liter, in Grams. |
|---|---|---|---|
| Acetylene ............. | $C_2H_2$ | 25.84 | 1.1611 |
| Ammonia.............. | $NH_3$ | 16.93 | 0.7607 |
| Carbon dioxide......... | $CO_2$ | 43.68 | 1.962 |
| "      monoxide...... | $CO$ | 27.80 | 1.249 |
| Chlorine ............. | $Cl_2$ | 70.36 | 3.1617 |
| Hydrochloric acid...... | $HCl$ | 36.18 | 1.625 |
| Hydrogen..........,.... | $H_2$ | 2. | 0.089873 |
| Methane............... | $CH_4$ | 15.92 | 0.7153 |
| Nitric oxide........... | $NO$ | 29.81 | 1.339 |
| Nitrogen.............. | $N_2$ | 27.86 | 1.252 |
| "      peroxide...... | $NO_2$ | 45.69 | 2.053 |
| Nitrous oxide.......... | $N_2O$ | 43.74 | 1.9655 |
| Oxygen............... | $O_2$ | 31.76 | 1.429 |
| Sulphur dioxide........ | $SO_2$ | 63.59 | 2.8575 |

Morley's values for oxygen and hydrogen were adopted, and the others calculated on this basis.

## APPROXIMATE COMPOSITION OF A NUMBER OF ALLOYS.

| | Proportions in which Combination takes Place. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Sn | Ni | Ag | P | Cd | Bi | Pb | Al | Sb |
| Brass............. | 66 | 33 | | | | | | | .3 | | |
| Gun-metal........ | 90 | | 10 | | | | | | | | |
| Bell-metal........ | 77 | | 23 | | | | | | | | |
| German silver..... | 60 | 20 | | 20 | | | | | | | |
| Silver coins....... | 10 | | | | 90 | | | | | | |
| Wood's metal...... | | | 13.5 | | | | 10 | 49.8 | 26.7 | | |
| Rose's metal...... | | | 25 | | | | | 50 | 25 | | |
| Britannia metal.... | 7–8 | 2 | 77–90 | | | | | | | | 10–15 |
| Pewter........... | 1 | | 2–20 | | | | | | | | |
| Aluminium bronze | 90 | | | | | | | | | 10 | |
| Art bronze ... ... | 86.6 | 3.3 | 6.6 | | | | | | 3.3 | | |
| Soft solder........ | | | 50 | | | | | | 50 | | |
| Babbitt metal..... | 3.7 | | 88.9 | | | | | | | | 7.4 |
| Nickel coins ...... | 75 | | | 25 | | | | | | | |
| Phosphor bronze .. | 90 | | 9 | | | 0.5 | | | | | |

## FREEZING-MIXTURES.

The mixtures given below will be found useful in cases where low temperatures are desired.

| | Temperature falls from | to |
|---|---|---|
| 1 pt. potassium sulphocyanate + 1 pt. water........ + 18 | | − 21 |
| 1 pt. sodium chloride + 3 pts. snow............... | | − 21 |
| 3 pts. crystallized calcium chloride + 1 pt. snow..... | | − 48.5 |
| 1 pt. snow + 1 pt. dilute sulphuric acid........ .... + 5 | | − 41 |
| 1 pt. potassium chloride + 4 pts. water............ | | − 11.8 |
| 3 pts. sodium nitrate + 4 pts. water................ + 13.2 | | − 5.3 |
| Solid carbonic acid + ether....................... | | − 100 |

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## TABLE OF WEIGHTS AND MEASURES.

### WEIGHT.

| | | |
|---|---|---|
| 1 gram | = | 15.432 grains ; |
| 1 grain | = | 0.06479 grams ; |
| 1 ounce avoirdupois | = | 28.3495 grams ; |
| 1 ounce troy | = | 31.1035 grams ; |
| 1 pound avoirdupois | = | 0.45359 kilogram ; |
| 1 pound troy | = | 0.37324 kilogram ; |
| 1 kilogram | = | 2.2046 pounds avoirdupois. |

### LENGTH.

| | | |
|---|---|---|
| 1 millimeter | = | 0.03937 inches ; |
| 1 inch | = | 25.3995 millimeters ; |
| 1 meter | = | 3.280899 feet ; |
| 1 foot | = | 0.30479 meter ; |
| 1 mile | = | 1609.31 meters. |

### VOLUME.

| | | |
|---|---|---|
| 1 cubic centimeter | = | 0.061027 cubic inches ; |
| 1 cubic inch | = | 16.386 cubic centimeters ; |
| 1 cubic centimeter | = | 0.03519 fluid ounce ; |
| 1 fluid ounce | = | 28.41 cubic centimeters ; |
| 1 liter | = | 1.76 pints ; |
| 1 liter | = | 0.2201 gallon ; |
| 1 gallon | = | 4.543 liters. |

# COMPARISON OF THE TWADDELL SCALE WITH THE BAUMÉ AND GAY-LUSSAC SCALES.

| Tw. | B. | G.-L. | Tw. | B. | G.-L. | Tw. | B. | G.-L. | Tw. | B. | G.-L. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 1.000 | 44 | 26.0 | 1.220 | 88 | 44.1 | 1.440 | 131 | 57.1 | 1.655 |
| 1 | 0.7 | 1.005 | 45 | 26.4 | 1.225 | 89 | 44.4 | 1.445 | 132 | 57.4 | 1.660 |
| 2 | 1.4 | 1.010 | 46 | 26.9 | 1.230 | 90 | 44.8 | 1.450 | 133 | 57.7 | 1.665 |
| 3 | 2.1 | 1.015 | 47 | 27.4 | 1.235 | 91 | 45.1 | 1.455 | 134 | 57.9 | 1.670 |
| 4 | 2.7 | 1.020 | 48 | 27.9 | 1.240 | 92 | 45.4 | 1.460 | 135 | 58.2 | 1.675 |
| 5 | 3.4 | 1.025 | 49 | 28.4 | 1.245 | 93 | 45.8 | 1.465 | 136 | 58.4 | 1.680 |
| 6 | 4.1 | 1.030 | 50 | 28.8 | 1.250 | 94 | 46.1 | 1.470 | 137 | 58.7 | 1.685 |
| 7 | 4.7 | 1.035 | 51 | 29.3 | 1.255 | 95 | 46.4 | 1.475 | 138 | 58.9 | 1.690 |
| 8 | 5.4 | 1.040 | 52 | 29.7 | 1.260 | 96 | 46.8 | 1.480 | 139 | 59.2 | 1.695 |
| 9 | 6.0 | 1.045 | 53 | 30.2 | 1.265 | 97 | 47.1 | 1.485 | 140 | 59.5 | 1.700 |
| 10 | 6.7 | 1.050 | 54 | 30.6 | 1.270 | 98 | 47.4 | 1.490 | 141 | 59.7 | 1.705 |
| 11 | 7.4 | 1.055 | 55 | 31.1 | 1.275 | 99 | 47.8 | 1.495 | 142 | 60.0 | 1.710 |
| 12 | 8.0 | 1.060 | 56 | 31.5 | 1.280 | 100 | 48.1 | 1.500 | 143 | 60.2 | 1.715 |
| 13 | 8.7 | 1.065 | 57 | 32.0 | 1.285 | 101 | 48.4 | 1.505 | 144 | 60.4 | 1.720 |
| 14 | 9.4 | 1.070 | 58 | 32.4 | 1.290 | 102 | 48.7 | 1.510 | 145 | 60.6 | 1.725 |
| 15 | 10.0 | 1.075 | 59 | 32.8 | 1.295 | 103 | 49.0 | 1.515 | 146 | 60.9 | 1.730 |
| 16 | 10.6 | 1.080 | 60 | 33.3 | 1.300 | 104 | 49.4 | 1.520 | 147 | 61.1 | 1.735 |
| 17 | 11.2 | 1.085 | 61 | 33.7 | 1.305 | 105 | 49.7 | 1.525 | 148 | 61.4 | 1.740 |
| 18 | 11.9 | 1.090 | 62 | 34.2 | 1.310 | 106 | 50.0 | 1.530 | 149 | 61.6 | 1.745 |
| 19 | 12.4 | 1.095 | 63 | 34.6 | 1.315 | 107 | 50.3 | 1.535 | 150 | 61.8 | 1.750 |
| 20 | 13.0 | 1.100 | 64 | 35.0 | 1.320 | 108 | 50.6 | 1.540 | 151 | 62.1 | 1.755 |
| 21 | 13.6 | 1.105 | 65 | 35.4 | 1.325 | 109 | 50.9 | 1.545 | 152 | 62.3 | 1.760 |
| 22 | 14.2 | 1.110 | 66 | 35.8 | 1.330 | 110 | 51.2 | 1.550 | 153 | 62.5 | 1.765 |
| 23 | 14.9 | 1.115 | 67 | 36.2 | 1.335 | 111 | 51.5 | 1.555 | 154 | 62.8 | 1.770 |
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